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10/02/2008

1. Document ID: US 20020061955 A1

L21: Entry 1 of 21

File: PGPB

May 23, 2002

PGPUB-DOCUMENT-NUMBER: 20020061955
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020061955 A1

TITLE: Emulsion styrene-butadiene rubber

PUBLICATION-DATE: May 23, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
<u>Colvin, Howard Allen</u>	Akron	OH	US	
Senyek, Michael Leslie JR.	Tallmadge	OH	US	

US-CL-CURRENT: 524/493; 524/502, 524/515, 526/303.1, 526/319, 526/335, 526/346

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	1000
Draw Desc	Image									

2. Document ID: US 6232404 B1

L21: Entry 2 of 21

File: USPT

US-PAT-NO: 6232404
DOCUMENT-IDENTIFIER: US 6232404 B1

TITLE: Elastomer blend and use in tires

DATE-ISSUED: May 15, 2001

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sandstrom; Paul Harry	Tallmadge	OH		
Blok; Edward John	Wadsworth	OH		
Zanzig; David John	Uniontown	OH		
<u>Colvin; Howard Allen</u>	Tallmadge	OH		
Senyek; Michael Leslie	Tallmadge	OH		

US-CL-CURRENT: 525/197; 152/450, 525/198, 525/240, 525/241

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	1000
Draw Desc	Image									

layer and comprised of monomeric or polymeric cationic quaternary compound; and mixtures thereof, and a lightfastness inducing agent, and wherein the cationic component or mixtures thereof are present in amounts of from about 80 parts by weight to about 97 parts by weight, the lightfastness inducing components are present in amounts of from about 20 parts by weight to about 3 parts by weight, and a third ink receiving layer situated on the top of the second cationic layer and comprised of block or graft polymers with at least two components, wherein one component is more compatible with the fast drying colored inks and is selected from the group consisting of monomeric polysaccharides and vinyl polymers, and the second component is more compatible with the slow drying black inks and is selected from the group consisting of alkylene oxide

* * * * *

polymers, formaldehyde resins, maleic anhydride, and maleic acid containing polymers, acrylic polymers, imine polymers, a biocide and a filler.
21. A transparency comprised of a supporting substrate, hereinafter and hereunder a first coating layer comprised of an anionic polymer, a second cationic coating layer situated on the top of the first anionic layer, and which second layer is comprised of monomeric or polymeric cationic quaternary compounds, and which second layer contains a lightfastness inducing agent, and a third ink receiving coating layer situated on the top of the second cationic layer, said third coating layer being comprised of a block polymer, a biocide and a filler.

3. Document ID: US 6166140 A

L21: Entry 3 of 21

File: USPT

US-PAT-NO: 6166140

DOCUMENT-IDENTIFIER: US 6166140 A

TITLE: Elastomer blend and use in tires

DATE-ISSUED: December 26, 2000

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Sandstrom; Paul Harry	Tallmadge	OH		
Blok; Edward John	Wadsworth	OH		
Zanzig; David John	Uniontown	OH		
Colvin; Howard Allen	Tallmadge	OH		
Senyek; Michael Leslie	Tallmadge	OH		

US-CL-CURRENT: 525/197; 152/450, 425/28.1, 425/340, 425/363, 525/198, 525/240, 525/241

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	FWMC
Draw Desc	Image									

4. Document ID: US 6066705 A

L21: Entry 4 of 21

File: USPT

US-PAT-NO: 6066705

DOCUMENT-IDENTIFIER: US 6066705 A

TITLE: Vapor phase synthesis of cis-1, 4-Polyisoprene

DATE-ISSUED: May 23, 2000

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Calderon; Nissim	Akron	OH		
Castner; Kenneth Floyd	Uniontown	OH		
Colvin; Howard Allen	Tallmadge	OH		
Muse, Jr.; Joel	Hudson	OH		

US-CL-CURRENT: 526/141; 524/722, 524/856, 526/129, 526/142, 526/159, 526/168, 526/340.2, 526/340.4, 526/88, 526/901, 528/501

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	FWMC
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5. Document ID: US 5986010 A

L21: Entry 5 of 21

File: USPT

US-PAT-NO: 5986010

DOCUMENT-IDENTIFIER: US 5986010 A

Jun. 30, 1981

Best Available Copy

[15]

Stoveken

[54] LAMINATED FOAM-CREPPED PAPER
PRODUCT AND METHOD OF
PRODUCTION THEREOF[76] Inventor: F. Raymond Stoveken, 28 Meadow
La., East Windsor, N.J. 08520

[21] Appl. No.: 99,513

[22] Filed: Dec. 3, 1979

[51] Int. Cl. B32B 3/28; B32B 5/20
U.S. Cl. 428/153; 428/156/79;
427/244; 427/373; 427/391; 428/314;
428/318; 428/514[58] Field of Search 428/153, 154, 314, 310,
428/514, 318; 156/79; 427/244, 373, 391

[56] References Cited

Politzer et al. 11/1973 3,607,341
Stokes 5/1918 1,265,132
Riley 9/1958 2,853,411
Aykanian 11/1962 3,062,698
Flanders 9/1965 3,205,120
Bartell et al. 11/1966 3,285,800
Maskey et al. 1/1968 3,365,532
Lewis, Jr. et al. 1/1969 3,424,643
Bernier 4/1970 3,506,533
Kell 5/1970 3,511,788
Adams et al. 9/1970 3,530,030
Frank 8/1971 3,600,262
Wolinski 8/1971 3,600,265
Goins et al. 9/1971 3,607,341
428/314
428/513
156/82
428/314
428/314
428/154
428/318
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428/314
428/314
428/314
428/314
162/112
156/79

U.S. PATENT DOCUMENTS

ABSTRACT

[57]

A laminated foam-crepped paper product and method of production thereof are disclosed. The laminated paper product exhibits increased wet strength and bulk and is highly absorbent, while also possessing cloth-like tactile properties. The foam layer is derived from an aqueous solution or dispersion of a film-forming material, and is caused to set soon after formation on the crepped paper layer to prevent release of the crepe while minimizing penetration of the foam into the crepped paper.

19 Claims, No Drawings

Primary Examiner—William J. Van Baten
Attorney, Agent, or Firm—Burns, Doane, Swecker & Mathis

FOREIGN PATENT DOCUMENTS

Sokolowski 7/1972 3,677,858
Wideman 8/1972 3,687,797
Shetton et al. 5/1974 3,813,262
Harrison 7/1974 3,822,176
Barron et al. 1/1975 3,862,879
Kapral 7/1975 3,895,154
Yoshitoka 12/1975 3,925,127
Hocoy 12/1976 4,000,028
Hocoy 4/1977 4,018,647
Hocoy 1/1978 4,069,366
Chapman et al. 2/1978 4,075,382
428/314
428/153
427/373
428/153
428/318
428/314
427/391
428/314
428/192

TITLE: Polymer for asphalt cement modification

DATE-ISSUED: November 16, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Clites; Jean Steininger	North Canton	OH		
<u>Colvin; Howard Allen</u>	Tallmadge	OH		
Klemmensen; Daniel Frederick	Tallmadge	OH		

US-CL-CURRENT: 525/250; 525/271, 525/314, 526/173, 526/175

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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KMC

6. Document ID: US 5955537 A

L21: Entry 6 of 21

File: USPT

US-PAT-NO: 5955537

DOCUMENT-IDENTIFIER: US 5955537 A

TITLE: Continuous polymerization process

DATE-ISSUED: September 21, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Steininger Clites; Jean	North Canton	OH		
<u>Colvin; Howard Allen</u>	Tallmadge	OH		
Fiedler; Ronald David	Atwater	OH		

US-CL-CURRENT: 525/53; 525/271, 525/316, 526/336, 526/65

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KMC

7. Document ID: US 5859156 A

L21: Entry 7 of 21

File: USPT

US-PAT-NO: 5859156

DOCUMENT-IDENTIFIER: US 5859156 A

TITLE: Vapor phase synthesis of rubbery polymers

DATE-ISSUED: January 12, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Calderon; Nissim	Akron	OH		
Muse, Jr.; Joel	Hudson	OH		
<u>Colvin; Howard Allen</u>	Tallmadge	OH		
Castner; Kenneth Floyd	Uniontown	OH		

comparisons to laminated non-creped paper products.

It is still yet another object of the present invention to provide a method for the production of a laminated foam-creped paper product which enables the paper product to be produced without significantly impairing its absorbency.

It is also another object of the present invention to provide a method for the production of a laminated foam-creped paper product which is simple and efficient. It is still another object of the present invention to obviate the disadvantages of the prior art as outlined above.

In one aspect of the present invention there is thus provided a method for the production of a laminated foam-creped paper product which exhibits improved wet strength and bulk, and is highly absorbent comprising:

forming an unset and ungelled foamed film of an aqueous dispersion or solution of a film-forming material on at least one surface of a layer of creped paper; and causing said foamed film to set or gel such that the amount of moisture absorbed by the paper from the film prior to said setting or gelling is insufficient to cause the crepe in the paper to be released, whereupon a laminate is formed having a set or gelled foamed film which is bonded to the creped paper.

In another aspect of the present invention there is provided a method for the production of a laminated foam-creped paper product which exhibits improved wet strength and bulk, and is highly absorbent comprising: forming an unset and ungelled foamed film of an aqueous dispersion or solution of a film-forming material between opposing surfaces of two layers of creped paper; and causing said foamed film to set or gel such that the amount of moisture absorbed by the paper from the film prior to said setting or gelling is insufficient to cause the crepe in the paper to be released, whereupon a laminate is formed having a set or gelled foamed film which bonds said layers of paper together.

In yet another aspect of the present invention, there are provided laminated foam-creped paper products produced according to either of the above methods.

DETAILED DESCRIPTION OF THE INVENTION

It has been found that the laminated foam-creped paper products of the present invention exhibit increased bulk and wet strength in comparison to conventional paper products comprised of non-creped paper. In addition, the products of the present invention are highly absorbent and exhibit a cloth-like tactile sensation due, in part, to the presence of the creping in the paper.

The laminated paper products of the present invention may take several forms. For example, the product may comprise a laminate of at least two layers of creped paper bonded together with a set or gelled foamed film derived from an aqueous solution or dispersion of a film-forming material located between the creped paper layers. The laminated product may also comprise a laminate of a single layer of creped paper having bonded to at least one surface thereof a set or gelled

LAMINATED FOAM-CREPED PAPER PRODUCT AND METHOD OF PRODUCTION THEREOF

BACKGROUND OF THE INVENTION

The present invention relates to improved laminated foam-creped paper products and methods of producing such laminates.

Laminated paper products which contain at least one layer of paper (either creped or non-creped) bonded to a foamed layer have been known for some time. Such products exhibit increased strength and bulk as compared to non-laminated products. For example, U.S. Pat. No. 3,687,797, issued to Wideman, discloses a resilient cellulosic wadding product useful as a disposable towel, washcloth, or covering which comprises an outer layer of cellulosic wadding (e.g. creped wadding) and a second outer layer of flexible, open-celled polymeric foam which is adhesively joined to said wadding.

U.S. Pat. No. 3,285,800, issued to Bartell et al, discloses a cushioning and wrapping laminate which consists of a sheet of polystyrene foam fused to a facing sheet of light cloth or creped paper. In addition, U.S. Pat. No. 3,530,030, issued to Adams et al, discloses a textile substitute comprising a substrate of a thin, flexible, permeable cellular polymeric material which is adhesively laminated to a paper sheet such as creped paper. U.S. Pat. No. 3,366,532, issued to Maskey et al, discloses an absorbent paper laminate wherein the paper layers are bonded together with regenerated cellulose in the form of a viscose foam. The laminate may be subjected to various finishing steps (e.g. creping) to impart specific characteristics to the product.

One disadvantage of certain of the laminated paper products of the above-discussed patents, however, is the use in their production of thermal fusion or an adhesive to bond a preformed foamed layer to the paper layer. Such methods of lamination are costly, time consuming, and can greatly affect the physical characteristics (e.g., absorbency and flexibility) of the laminated product. In addition, the use of a creping procedure as a finishing step to impart specific surface characteristics to a laminated foam-paper product results in the destruction of portions of the foam structure, decreasing the absorbency and flexibility of the laminate, as well as affecting the tactile properties thereof.

It is therefore highly desirable to provide a more efficient and effective process for the production of a laminated paper product which will provide a product having high absorbency and flexibility as well as enhanced cloth-like tactile properties and wet strength in comparison to conventional laminated products of either creped or non-creped paper.

OBJECTS AND SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a laminated foam-creped paper product which is highly absorbent.

It is another object of the present invention to provide a laminated foam-creped paper product having cloth-like tactile properties.

It is yet another object of the present invention to provide a laminated foam-creped paper product which is highly flexible.

It is still yet another aspect of the present invention to provide a laminated foam-creped paper product which exhibits improved absorbency, wet strength, and tactile

US-CL-CURRENT: 526/64, 524/722, 524/741, 524/856, 526/129, 526/133, 526/137, 526/141,
526/142, 526/169.1, 526/340.2, 526/340.4, 526/68, 526/69, 526/88, 526/901, 526/903

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWWC

8. Document ID: US 5837756 A

L21: Entry 8 of 21

File: USPT

US-PAT-NO: 5837756

DOCUMENT-IDENTIFIER: US 5837756 A

TITLE: Polymer for asphalt cement modification

DATE-ISSUED: November 17, 1998

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Steininger Clites; Jean	North Canton	OH		
<u>Colvin; Howard Allen</u>	Tallmadge	OH		
Klemmensen; Daniel Frederick	Tallmadge	OH		

US-CL-CURRENT: 524/68; 525/316

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWWC

9. Document ID: US 5652304 A

L21: Entry 9 of 21

File: USPT

US-PAT-NO: 5652304

DOCUMENT-IDENTIFIER: US 5652304 A

TITLE: Vapor phase synthesis of rubbery polymers

DATE-ISSUED: July 29, 1997

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Calderon; Nissim	Akron	OH		
Castner; Kenneth Floyd	Uniontown	OH		
<u>Colvin; Howard Allen</u>	Tallmadge	OH		
Muse, Jr.; Joel	Hudson	OH		

US-CL-CURRENT: 526/142, 524/722, 524/741, 524/856, 526/129, 526/137, 526/141, 526/159,
526/168, 526/169.1, 526/340.2, 526/340.4, 526/88, 526/901, 526/903

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Drawn Desc	Image								

KWWC

10. Document ID: EP 926192 A1

foamed film derived from an aqueous solution or dispersion of a film-forming material.

Any suitable type of paper substrate (e.g., in the form of separate layers or webs) may be used as long as the paper is creped or may have a crepe imparted thereto prior to formation of the foam thereon. The presence of the crepe in the paper enables the laminated product to exhibit high wet strength and absorbency as well as provide a highly desirable cloth-like tactile sensation (especially in a wet state). It has been found that the presence of the crepe in the paper substrate also greatly enhances the flexibility of the laminated paper product, thus enabling a product to be produced which exhibits cloth-like draping characteristics. The enhanced flexibility is due to the fact that as the product is subjected to bending, the stresses which act upon the side of the laminate being stretched are compensated for by corresponding stretch within the crepe of the paper. The crepe exhibits some resiliency and will thus substantially return to its original form upon cessation of the bending forces due to the bonding between the foam matrix (formed upon setting or gelling of the foamed layer) and the creped paper. This characteristic of the crepe allows the laminated product to exhibit cloth-like flexibility and draping characteristics when dry as well as being soft and possessing excellent drapability when wet.

The foam-creped paper laminate of this invention is also highly absorbent due to the fact that the creping effect greatly increases the bulk as well as the surface area of the paper. As a direct result, high absorbency is exhibited due to the capillary action of the creped paper. It is therefore essential that the creped paper which is employed in the laminated paper product of the present invention retain its crepe subsequent to the formation of the foam on the paper.

The creped paper which is employed in the present invention may be produced by conventional methods. For example, the paper may consist of "dry crepe" paper produced by a dry creping process (e.g., using the Yankee-Foundry process). The crepe paper may also consist of "wet crepe" paper produced by passing moistened paper over a roll equipped with a doctor blade which imparts a crepe to the paper.

The crepe paper may be of any suitable thickness and bulk. For example, lightweight paper such as creped tissue paper may advantageously be employed in the laminated product of the present invention. Tissue weight paper generally has a single ply weight of about 7 to 18 pounds per ream. Towel weight paper may also be used and generally has a single ply weight of about 15 to 75 pounds per ream. Single or multi-ply paper may be used. The paper layer is also preferably untreated, i.e., the surface characteristics of the paper need not be modified prior to the preparation of the laminate by application of water repellent agents or the like.

For normally contemplated uses, the crepe paper employed in the product of this invention will generally have a thickness ranging from about 2 mils to about 30 mils. A particularly advantageous thickness (i.e., the thickness of tissue paper) ranges from about 2 to 6 mils, and is most preferably about 3 mils.

The film-forming material from which the foamed film layer is formed may be selected from a wide variety of conventional water-soluble or water-dispersible materials. However, the aqueous solution or dispersion of the film-forming material must be capable of being foamed, with the resulting foam then being set or gelled.

(i.e., stabilized) to produce a foamed layer on the surface becomes bonded to the creped paper during the setting or gelling process.

For example, the foamed layer may be made from conventional synthetic latexes comprised of various polymers and copolymers. Exemplary polymers and copolymers include those made from styrene, vinylidene chloride, acrylonitrile, butadiene, urethane, vinyl esters, and acrylic esters. Cellulose derivatives such as methyl cellulose, carboxymethyl cellulose, and cellulose ether may be employed in an aqueous solution to provide a foamable aqueous solution. Other desirable film-forming materials which are suitable for use in the present invention include polyacrylic acid salts, polyacrylamide, and acrylamide copolymers. Additional desirable film-forming materials include polyethylene oxide, polyvinyl alcohol, polyvinylpyrrolidone, starch and its derivatives, casein, and guar gum. This listing is not all-inclusive and one of ordinary skill in the art would readily understand which materials were appropriate for use in the present invention. Blends of suitable film-forming materials may also be employed in a foamable dispersion or solution.

Aqueous dispersions of synthetic latexes are marketed commercially. Such latex dispersions are either non-cross-linking, self cross-linking, or cross-linkable. The trade-names Geon and Hycar by the B. F. Goodrich Chemical Company. The formulation of such dispersions and solutions is well within the skill of the practitioner in the art.

The density of the foamed aqueous dispersion or solution of the film-forming material will generally range from about 0.05 to about 0.50 grams/cc. Various fillers such as bentonite clay, kaolin clay, diatomaceous earth, or colloidal silica may be added to the foamed solution in order to increase the solids content and the density thereof if desired.

Other conventional additives may be used in conventional amounts in order to modify specific characteristics of the foam. Thickeners such as cellulose derivatives may be used to increase the viscosity of the solution without materially additionally increasing the solids content thereof. Foam stabilizers, dyes, pigments, plasticizers, flame retardants, and curing agents (if required) may also be employed. Exemplary pigments may include clays, titanium dioxide, carbon black, graphite, and colored lakes and toners. Suitable foaming agents and stabilizers include ammonium stearate, sodium lauryl sulfate, etc.

The penetration of moisture into the creped paper from the foamed aqueous dispersion or solution during formation of the laminate should be minimized to prevent excessive absorption of moisture by the paper prior to the setting or gelling of the foam. While some moisture will inherently penetrate the creped paper upon contact with the foam due to the inherent porosity of the paper, the presence of excessive moisture in the creped paper will disadvantageously cause the crepe in the paper to be released. That is, if an excessive amount of moisture is absorbed by the paper, the paper will eventually stretch to such an extent that the creped configuration which is essential to the practice of the present invention.

Normally, the crepe in the paper will begin to be released when the moisture content of the paper reaches about 7 to 10 percent by weight, depending upon what

L21: Entry 10 of 21

File: EPAB

Jun 30, 1999

PUB-NO: EP000926192A1
DOCUMENT-IDENTIFIER: EP 926192 A1
TITLE: Rubber blend for tire tread compounds

PUBN-DATE: June 30, 1999

INVENTOR-INFORMATION:

NAME	COUNTRY
COLVIN, HOWARD ALLEN	US
SENYEK, MICHAEL LESLIE	US
FUTAMURA, SHINGO	US

INT-CL (IPC): C08 L 9/00; C08 L 9/06; C08 K 3/36; B60 C 1/00
EUR-CL (EPC): C08L009/00; B60C001/00, C08K003/36, C08L009/06

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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11. Document ID: US 5859156 A

L21: Entry 11 of 21

File: EPAB

Jan 12, 1999

PUB-NO: US005859156A
DOCUMENT-IDENTIFIER: US 5859156 A
TITLE: Vapor phase synthesis of rubbery polymers

PUBN-DATE: January 12, 1999

INVENTOR-INFORMATION:

NAME	COUNTRY
CALDERON, NISSIM	US
MUSE, JR JOEL	US
COLVIN, HOWARD ALLEN	US
CASTNER, KENNETH FLOYD	US

INT-CL (IPC): C08 F 2/34; C08 F 136/06; C08 F 136/08
EUR-CL (EPC): C08F136/06; B01J008/10, B01J008/24, C08F036/04, C08F136/08

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWC

12. Document ID: EP 881242 A2

L21: Entry 12 of 21

File: EPAB

Dec 2, 1998

PUB-NO: EP000881242A2
DOCUMENT-IDENTIFIER: EP 881242 A2
TITLE: Polymer for asphalt cement modification

PUBN-DATE: December 2, 1998

INVENTOR-INFORMATION:

degree of foam, the paper must be heated to a temperature which will cause the crepe to be released, depending upon the type of paper employed. It is therefore desirable to reduce the moisture content of the dispersion or solution of the film-forming material to only that moisture content required to permit stable foaming so that excessive moisture will not be present which could release the crepe upon being absorbed by the paper. Generally, the moisture content of the dispersion or solution will range from about 20 to about 80 percent by weight. However, the moisture content of the dispersion or solution can range as low as about 5 percent by weight based upon the weight of the dispersion or solution and still enable a foam to be formed therefrom. A preferred moisture content of the film-forming material is about 20 to about 60 percent by weight. Concomitantly, the solids content (i.e., the amount of non-volatile components present) will generally range from about 20 to about 95 percent by weight based upon the weight of the solution or dispersion. The moisture content depends upon the specific materials used, with a higher solids content of the foam correspondingly decreasing the percentage moisture content of the foam. The penetration (i.e., the absorption) of moisture into the paper may be controlled and minimized in several other ways. The creped paper may be dried prior to being employed in the production of the laminated product in order to reduce the inherent moisture content of the paper. For example, the inherent moisture content may be reduced from a normal content of about 3 to about 12 percent by weight (depending upon conditions of temperature and humidity) to about 2 percent by weight by drying the paper prior to formation of the laminate. In this manner, the paper may thereafter absorb amounts of moisture ranging up to about 5 to about 8 percent by weight in addition to that which it already contains, thus providing a total moisture content of from about 7 to about 10 percent by weight or less, without causing the crepe in the paper to be released. Naturally, a light weight creped paper sheet (e.g., tissue weight paper) will normally be able to absorb less moisture on a per weight basis than a heavier weight creped paper (e.g., towel weight paper) before the crepe in the crepe is released. In addition, creped paper produced from a dry creping process is more sensitive to moisture absorption than crepe paper produced from a wet creping process. That is, the creped paper from the wet creping process will be able to absorb more moisture on a per weight basis than the paper produced from a dry creping process without releasing the crepe. The laminated paper product of the present invention may thus be produced by preparing the aqueous dispersion or solution of the film-forming material, forming a foam from the dispersion or solution, applying the foam in an unset or ungelled state to the desired creped paper substrate, and causing the foamed film to set or gel such that the amount of water absorbed by the paper is insufficient to cause the crepe in the paper to be released. The foam may be applied between opposing surfaces of two layers or webs of creped paper by suitable means (e.g., by extrusion), with the two layers or webs then being sufficiently brought together by suitable means to form the laminate without causing a significant collapse of the foam (e.g., by means of controlled gap rollers). The foam may also be applied to one or both sides of a single layer or web of creped paper. The foam is then heated to a temperature ranging from about 100 to about 400° F.

Most preferably, the foamed film is caused to set substantially immediately upon being formed on the paper to ensure that the paper does not absorb sufficient moisture from the film prior to the setting or gelling thereof to cause the crepe in the paper to be released. The foamed layer may be encouraged to set or gel substantially immediately upon being formed on the creped paper by preheating the paper prior to the formation of the foamed film. Such preheating will also serve to dry the laminated product and prevent excessive moisture absorption. The paper, if preheated, will generally be heated to temperatures ranging from about 100 to about 400° F.

If a laminated product is desired which comprises only one layer of creped paper which is covered on either one or both sides with a set or gelled foam layer, the dispersion or solution may be applied to the surface of a web (in either a foamed or unfoamed state) and proportioned by suitable means (e.g., by the knife-over-roll technique) prior to setting or gelling the foam. Generally any suitable conventional equipment may be used to physically apply the unset or ungelled dispersion or solution of the film-forming material which enables it to be deposited and uniformly spread across the surface of the creped paper to form a film thereon. The determination of which equipment is suitable for the deposition of the dispersion or solution (in either a foamed or unfoamed state) is well within the skill of the artisan.

The foam may be formed prior to application to the paper by entraining sufficient air into the aqueous solution or dispersion by suitable means. A preferred method of providing a foamed aqueous dispersion or solution of the film-forming material is by mechanically whipping air into the dispersion or solution until a suitable foam is provided.

The paper product of the present invention may also be produced by incorporating a suitable foaming agent into the aqueous dispersion or solution of the film-forming material, applying the solution or dispersion (in an unfoamed state) to the paper substrate as described above, forming the foam by action of the foaming agent together with any necessary heating, and causing the foamed film which is formed to set for gel. The use of such foaming agents is known and it is within the skill of the artisan to form the foam in this manner.

If a foaming agent is used to form the foam, the foam should be formed as soon as possible subsequent to the application of the aqueous solution or dispersion to the creped paper substrate in order to minimize the penetration of moisture into the paper during the formation of the laminate. Preferably, the foam is formed substantially immediately upon application of the aqueous solution or dispersion to the substrate by application of heat to activate the foaming agent.

The foam which is formed will generally have a thickness of up to about 1000 mils, preferably from about 1 mil to about 125 mils, and most preferably from about 10 to about 50 mils upon being set or gelled. The thickness of the foam layer should be sufficient to impart the desired properties of bulk, wet strength, and absorbency to the laminated product upon being set or gelled.

NAME	COUNTRY
CLITES, JEAN STEININGER	US
COLVIN, HOWARD ALLEN	US
KLEMMENSEN, DANIEL FREDERICK	US

INT-CL (IPC): C08 F 297/04; C08 L 95/00
EUR-CL (EPC): C08F297/04; C08L095/00

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

RWD

13. Document ID: US 5652304 A

L21: Entry 13 of 21

File: EPAB

Jul 29, 1997

PUB-NO: US005652304A
DOCUMENT-IDENTIFIER: US 5652304 A
TITLE: Vapor phase synthesis of rubbery polymers

PUBN-DATE: July 29, 1997

INVENTOR-INFORMATION:

NAME	COUNTRY
CALDERON, NISSIM	US
CASTNER, KENNETH FLOYD	US
COLVIN, HOWARD ALLEN	US
MUSE, JR JOEL	US

INT-CL (IPC): C08 F 2/34; C08 F 136/06; C08 F 136/08
EUR-CL (EPC): B01J008/10; B01J008/24, C08F036/04 , C08F136/06 , C08F136/08 , G09F013/28 , G09F021/06

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

RWD

14. Document ID: WO 9708211 A1

L21: Entry 14 of 21

File: EPAB

Mar 6, 1997

PUB-NO: WO009708211A1
DOCUMENT-IDENTIFIER: WO 9708211 A1
TITLE: VAPOR PHASE SYNTHESIS OF RUBBERY POLYMERS

PUBN-DATE: March 6, 1997

INVENTOR-INFORMATION:

NAME	COUNTRY
CALDERON, NISSIM	
CASTNER, KENNETH FLOYD	
COLVIN, HOWARD ALLEN	
MUSE, JOEL JR	

INT-CL (IPC): C08 F 2/06; C08 F 2/34
EUR-CL (EPC): B01J008/10; C08F036/04, C08F136/06 , C08F136/08 , B01J008/24 , G09F013/28 , G09F021/06

The paper web, in the form of a web, may also be passed through controlled nip rollers which are preheated to provide a somewhat instantaneous heating effect to quickly set or gel the foam and initiate the setting process. Microwave or dielectric heating may also be employed in an attempt to set the foam substantially immediately upon application or formation. However, the creped paper should not be heated to such an extent that the foam will break down as it contacts the paper due to the surface temperature of the paper.

Laminates formed from the paper sheets which are creped (issue paper) may advantageously be dried subsequent to the formation of the foamed layer thereon to prevent an excessive amount of moisture from being absorbed by the paper. Such drying would normally be in addition to a setting or gelling step. On the other hand, a heavier weight sheet may not have to be dried (i.e., the foam need only be set or gelled), since the total amount of water which is absorbed by the paper may be insufficient to cause a release of the crepe.

If it is desired to dry the laminate subsequent to its formation (e.g., in the case of tissue weight creped paper where the excessive absorption of moisture may be a problem), any suitable method may be used. For example, the laminate may be passed through a drying chamber wherein heated air is directed onto the laminate. Typical drying temperatures (i.e., in the case of hot air or an oven) will generally range from about 200° F. to about 650° F. depending upon the residence time of the laminate in the oven. In such cases, the laminate is dried soon enough after its formation to avoid substantial penetration of moisture into the paper web so as to prevent a significant release of the crepe.

The time within which significant drying must occur under these circumstances will vary depending upon the moisture content of the foam, the viscosity of the dispersion or solution, the porosity of the paper, the thickness of the foam layer, etc. Naturally, the use of a highly porous creped paper or a foam having a high moisture content could necessitate that the laminate be dried fairly soon after being formed. It is also possible that the foam will be caused to set or gel during the drying process depending upon the specific drying temperatures and type of foam employed. The drying rate is determined so as to avoid such rapid removal of moisture from the foam such that the structure of the foam is destroyed.

It should be noted that as the foam begins to set and a foamed film which is bonded to the layer or layers of the paper substrate, the resulting matrix structure of the foam will impart some rigidity to the creped paper and thereafter inhibit the crepe from being released (i.e., by inhibiting the paper from stretching). After that point has been reached, the absorption of excessive moisture by the paper will no longer be a problem. That is, the paper can then absorb moisture in amounts greater than the amounts which would normally cause the crepe to be released. It is thus highly desirable to cause the foam to set as soon as possible subsequent to being formed upon a surface of the creped paper.

When a paper product is produced comprising two layers of creped paper bonded together by a foamed layer, it may be advantageous to feed a scrim web between the separate layers (in the form of webs) of creped paper along with the dispersion or solution as the webs pass between controlled nip rollers. In this way, a laminated paper product is produced having two outer creped paper layers bonded together with a thin foamed film having disposed therein a scrim layer. The product and permits the product to be used under conditions wherein greater amounts of stress may be placed upon the product without any tearing of the laminate taking place.

The present invention is additionally illustrated in connection with the following Examples which are to be considered illustrative of the present invention but should not be considered limiting thereof.

TABLE I

Foam Formulation (Wt. grams)			
X		Y	
Hycar 1572 \times 45 ¹	214.0	214.0	1.0
Triox X-100 ²	1.0	1.0	12.0
Ammonium stearate ³	40.0	40.0	140.0
Cellulose GP-52,000 ⁴	10.0	10.0	65.1
Percent Solids ⁵	32.5	32.5	

¹Nitric latex composition marketed by B. F. Goodrich Chemical Co.

²Surfactant marketed by Rohm and Haas

³Emulsion grade marketed by Procter and Gamble Co.

⁴Clay filler marketed by Engelhard Minerals and Chemicals Co.

⁵Thickening agent marketed by Union Carbide

⁶Percent solids is defined as the ratio of non-volatile components to the total weight of the formulation $\times 100$.

TABLE II

Summary of Conditions of Coating Runs			
Example	Foam Formulation ^a	Wet Foam Density (g/cc)	Setting (in)
1	Y	0.23	0.020
50	Web Speed (ft/min)	Cap	50

The foamed dispersions which are used in the preparation of the foam-creped paper laminates of Examples I to 4 of Tables II and III are prepared by pre-mixing all materials except for the clay filler and stirring the admixed materials for approximately five minutes. The clay filler is then slowly added and the dispersion mixed for an additional five minutes. The dispersion is frothed (i.e., foamed) by whipping at high speed in a Hobart mixer for four minutes followed by whipping at low speed for two minutes. Either of the foamed dispersions (i.e., X or Y) is then fed between opposing surfaces of advancing webs of single ply tissue weight creped paper as the webs pass between application rollers set to a desired gap between 0.020 and 0.040 inches. Approximately 6 seconds later, the coated webs pass through a drying oven wherein hot air at a temperature of 320° F. and a velocity of 1400 ft/minute impinges upon the webs to dry the laminate and set the foam. The webs are heated to about 200° F. as they pass through the oven. The residence time of any specific portion of a web as it passes through the oven is about 15 seconds. The laminated product which exits from the drying oven consists of two webs of creped tissue paper bonded together with a layer of dried set or gelled foam.

The specific conditions employed during the various Examples and the characteristics of the laminated foam-creped paper products produced therein are set forth in the following Tables:

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Clip Img	Image							

KMD

15. Document ID: EP 537640 A1

L21: Entry 15 of 21

File: EPAB

Apr 21, 1993

PUB-NO: EP000537640A1

DOCUMENT-IDENTIFIER: EP 537640 A1

TITLE: Polymers derived from a conjugated diolefin, a vinyl-substituted aromatic compound, and olefinically unsaturated nitrile.

PUBN-DATE: April 21, 1993

INVENTOR-INFORMATION:

NAME

SENYEK, MICHAEL LESLIE

COLVIN, HOWARD ALLEN

COUNTRY

US

US

US-CL-CURRENT: 526/340

INT-CL (IPC): C08F 236/12; C08L 21/00; C08L 55/02

EUR-CL (EPC): C08F236/12; C08L021/00

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KMD

16. Document ID: EP 537619 A1

L21: Entry 16 of 21

File: EPAB

Apr 21, 1993

PUB-NO: EP000537619A1

DOCUMENT-IDENTIFIER: EP 537619 A1

TITLE: Compatibilized polymeric systems.

PUBN-DATE: April 21, 1993

INVENTOR-INFORMATION:

NAME

COLVIN, HOWARD ALLEN

ALSAMARRAIE, MUHANAD AHMAD

PARKER, DANE KENTON

COUNTRY

US

US

US

US-CL-CURRENT: 524/507

INT-CL (IPC): C08G 18/10; C08G 18/40; C08G 18/72; C08L 21/00; C08L 67/00; C08L 77/00; C08L 101/02

EUR-CL (EPC): C08G018/40; C08G018/40, C08G018/72 , C08L067/00 , C08L077/00 , C08L079/02 , C08L101/00 , C08L019/00

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KMD

17. Document ID: EP 385918 A1

TABLE II-continued
Summary of Conditions of Coating Runs

Example	Foam	Wet Foam	Setting (min)	Speed (ft/min)
1	X	0.09	0.030	50
2	Y	0.23	0.030	50
3	X	0.09	0.030	50
4	X	0.09	0.040	50

TABLE III
Characteristics of Foam-Creped Paper Laminates

Example	Laminate Thickness (in)	Absorbency (lb/in)	Tensile Strength ^a	
			Dry	Wet
1	0.018	0.191	7.9	2.2
2	0.014	0.200	8.1	2.3
3	0.027	0.260	6.8	1.7
4	0.016	0.197	7.3	1.9
Control	0.006	0.196	4.7	1.2

The absorbency of each of the laminates produced is measured by immersing a 2 by 2 inch square portion of each laminate in water for ten seconds. The portion is then removed, allowed to drain for 3 to 4 seconds in a vertical position, and then weighed. The wet weight of the laminate is then compared to the dry weight of the laminate prior to immersion and absorbency determined.

The tensile strength of each of the laminates is measured in TAPPI standards T-404 TS-66 (for dry tensile strength) and T-456 OS-68 (for wet tensile strength).

As may be seen from the data contained within Table III, the foam-creped paper laminates of the present invention exhibit tensile strengths (both dry and wet) which are significantly greater than the tensile strengths exhibited by the control 2-ply tissue weight creped paper. The differences in wet tensile strength are particularly noteworthy. As an additional advantage, an increase in absorbency on a per square inch basis can also be achieved with the laminated products of the present invention in comparison with the control (2-ply tissue weight paper).

COMPARATIVE EXAMPLES A-D

In order to more clearly demonstrate the advantages of employing creped paper in the products of the present invention, foam-paper laminates are prepared using non-creped tissue weight paper. Foam formulation Y, the composition of which is described in Table I, is used to form the laminates of Comparative Examples A, B, C and D. These laminates are prepared by passing two separate layers of 2-ply tissue weight non-creped paper between controlled gap rollers set at a gap of 0.015 inch for Comparative Example A and 0.030 inch for Comparative Examples B, C and D. Three different types of non-creped tissue weight paper are employed. The foam formulation (in an unset state) is placed between the two separate layers of single ply paper prior to their passage between the rollers. The laboratory-prepared laminates thus formed are heated in an oven at 225° F. for five minutes in order to set (i.e., cure) the foam. The

TABLE IV
Characteristics of the Laminates Produced

Comparative Example	Laminate Thickness (in)	Absorbency (lb/in)	Tensile Strength	
			Dry	Wet
A ^a	0.020	0.083	6.3	0.5
B ^b	0.040	0.270	5.7	0.3
C ^c	0.038	0.260	7.9	0.8
D ^c	0.003	0.092	6.4	0.4

A comparison of Tables III and IV indicates that the use of creped paper as opposed to non-creped paper in the production of the paper laminates of the present invention provides several advantages.

For instance, while the tensile strength of each of the dry laminates produced from either creped or non-creped paper is generally greater than the tensile strength of each dry control paper (creped or non-creped), only the laminates which contain creped paper exhibit a significant increase in either dry or wet tensile strength. Surprisingly, the wet tensile strength of the laminates which contain non-creped paper differs little from the wet tensile strength of the laminates of the present invention (which contain creped paper) all exhibit significant increases over the wet tensile strength of the control creped paper. In fact, the increases in wet tensile strength range from about 50 percent to about 100 percent.

Such comparisons are even more striking when it is noted that the laminates of Comparative Examples B, C and D are much greater in cross-sectional thickness than the laminates of Examples 1 to 4 (i.e., from about 1.5 to about 2.5 times greater in thickness). This significant increase in thickness (which consists of additional foam) does not enhance the wet tensile strength characteristics of the laminates which employ a non-creped paper. To the contrary, the wet tensile strength of the laminates remains basically unchanged in relation to the wet tensile strength of the control paper. The laminates of the present invention are thus able to achieve desirable values for wet tensile strength without requiring a great increase in the bulk or weight of the paper laminate. In addition, it should be noted that the laminate of Comparative Example A, whose thickness substantially corresponds to the thickness of the laminate of Example I exhibits an absorbency (on the basis of surface area)

L21: Entry 17 of 21

File: EPAB

Sep 5, 1990

PUB-NO: EP000385918A1
DOCUMENT-IDENTIFIER: EP 385918 A1
TITLE: Crosslinkable rubber composition.

PUBN-DATE: September 5, 1990

INVENTOR-INFORMATION:

NAME

WEINSTEIN, ARTHUR HOWARD

COLVIN, HOWARD ALLEN

PARKER, DANE KENTON

COUNTRY

US

US

US

US-CL-CURRENT: 525/123

INT-CL (IPC): C08C 19/30; C08G 18/69; C08G 18/72; C08J 3/24

EUR-CL (EPC): C08C019/30; C08G018/69, C08G018/72 , C08J003/24

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWIC

18. Document ID: EP 357534 A1

L21: Entry 18 of 21

File: EPAB

Mar 7, 1990

PUB-NO: EP000357534A1
DOCUMENT-IDENTIFIER: EP 357534 A1
TITLE: Rubber vulcanization agents.

PUBN-DATE: March 7, 1990

INVENTOR-INFORMATION:

NAME

COLVIN, HOWARD ALLEN

BULL, CHARLES LEE JR

MAGNUS, FREDRICK LEWIS

COUNTRY

INT-CL (IPC): C07C 321/00; C08K 3/36

EUR-CL (EPC): C07G017/00; C08K005/36

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWIC

19. Document ID: EP 333626 A1

L21: Entry 19 of 21

File: EPAB

Sep 20, 1989

PUB-NO: EP000333626A1
DOCUMENT-IDENTIFIER: EP 333626 A1
TITLE: Ames-negative diamine curative for polyurethanes.

PUBN-DATE: September 20, 1989

INVENTOR-INFORMATION:

NAME

COLVIN, HOWARD ALLEN

COUNTRY

which is significantly lower than the absorbency of the laminates of Examples 1 to 4 (which employ creped paper). In fact, the laminate of Comparative Example A exhibits an absorbency which is less than half of the absorbency of any of the laminates of Examples 1 to 4, regardless of the thickness of the laminate. The thicknesses of the laminates employing non-creped paper had to be doubled to achieve a comparable absorbency. Note, in this regard, Comparative Examples B, C and D.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

What is claimed is:

1. A method for the production of a laminated foam-creped paper product which exhibits improved wet strength and bulk, and is highly absorbent comprising: forming an unset and ungelled foamed film of an aqueous dispersion or solution of a film-forming material on at least one surface of creped paper; and causing said foamed film to set or gel such that the amount of moisture absorbed by the paper from the film prior to the setting or gelling of the film is insufficient to cause the crepe in the paper to be released whereupon a laminate is formed having a set or gelled foamed film having a thickness of from about 1 to about 125 mils which is bonded to said creped paper.
2. The method of claim 1 wherein said creped paper comprises creped tissue paper.
3. The method of claim 1 wherein said creped paper comprises towel weight creped paper.
4. The method of claim 1 wherein said foamed film is caused to set or gel substantially immediately upon formation by preheating said paper prior to the forming of a film thereon so that the film will begin to set or gel as it contacts the heated paper.
5. The method of claim 1 wherein said foamed film is caused to set or gel by heating said laminate subsequent to the formation of the film thereon.
6. The method of claim 1 wherein said foamed film is formed on at least one surface of said creped paper by forming said aqueous dispersion or solution and applying the foamed dispersion or solution to the paper.
7. The method of claim 1 wherein said film is formed on at least one surface of said creped paper by applying

8. A method for the production of a laminated creped paper and thereafter foaming the dispersion or solution, said unset and ungelled dispersion or solution to the paper product which exhibits improved wet strength and bulk, and is highly absorbent comprising: forming an unset and ungelled foamed film of an aqueous dispersion or solution of a film-forming material between opposing surfaces of two layers of creped paper; and causing said foamed film to set or gel such that the amount of moisture absorbed by the paper prior to the setting or gelling of the film is insufficient to cause the crepe in the paper to be released whereupon a laminate is formed having a set or gelled foamed film which bonds said layers of paper together.

9. The method of claim 8 wherein said layers of creped paper comprise creped tissue paper.

10. The method of claim 8 wherein said layers of creped paper comprise towel weight creped paper.

11. The method of claim 8 wherein said foamed film is caused to set substantially immediately upon formation by preheating said creped paper prior to the forming of the film thereon so that the film will begin to set or gel as it contacts the heated paper.

12. The method of claim 8 wherein said foamed film is caused to set by heating said laminate subsequent to the formation of the film thereon.

13. The method of claim 8 wherein said foamed film is formed between opposing surfaces of two layers of creped paper by foaming said aqueous dispersion or solution and applying the foamed dispersion or solution between said opposing surfaces.

14. The method of claim 8 wherein the film is formed between said opposing surfaces.

15. A laminated paper product produced according to the method of claim 1.

16. A laminated paper product produced according to the method of claim 8.

17. The method of claim 1 wherein the thickness of the set or gelled foam film ranges from about 10 to about 50 mils.

18. The method of claim 8 wherein the thickness of the set or gelled foam film ranges from about 1 to about 125 mils.

19. The method of claim 18 wherein the thickness of the set or gelled foam film ranges from 10 to about 50 mils.

* * *

INT-CL (IPC): C08G 18/10; C08G 18/38; C08G 18/65
EUR-CL (EPC): C08G018/10; C08G018/65, C08G018/66

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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KWC

☒ 20. Document ID: EP 324312 A2

L21: Entry 20 of 21

File: EPAB

Jul 19, 1989

PUB-NO: EP000324312A2
DOCUMENT-IDENTIFIER: EP 324312 A2
TITLE: Polymer alloy.

PUBN-DATE: July 19, 1989

INVENTOR-INFORMATION:

NAME

MUSE, JOEL JR

COLVIN, HOWARD ALLEN

COUNTRY

INT-CL (IPC): C08L 21/00; C08L 23/02; C08L 23/36
EUR-CL (EPC): C08F008/34; C08L021/00, C08L021/00 , C08L021/00 , C08L023/32 , C08L023/32

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWC

☐ 21. Document ID: EP 258168 A1

L21: Entry 21 of 21

File: EPAB

Mar 2, 1988

PUB-NO: EP000258168A1
DOCUMENT-IDENTIFIER: EP 258168 A1
TITLE: Rubber vulcanization agents and methods for their preparation.

PUBN-DATE: March 2, 1988

INVENTOR-INFORMATION:

NAME

COLVIN, HOWARD ALLEN

BULL, CHARLES LEE JR

COUNTRY

INT-CL (IPC): C07C 149/00; C08K 3/36
EUR-CL (EPC): C08K005/36; C07G017/00

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWC

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|------|---|
| [54] | SURFACE PROTECTIVE COATING ON AN ARTICLE AT LEAST SURFACE OF WHICH IS FORMED OF A SYNTHETIC RESIN |
| [75] | Inventors: Kyoeichi Shukuri, Amagasaki; Kenzo Sono, Nishinomiya, both of Japan |
| [73] | Assignees: Nippon Sheet Glass Co., Ltd.; Nippon Hydon Co. Ltd., both of Japan |
| [22] | Filed: Feb. 28, 1973 |
| [21] | Appl. No.: 336,805 |
| [30] | Foreign Application Priority Data |

- [52] U.S. CI. 428/206; 350/61; 351/62;
351/166; 427/39; 427/42; 427/50; 427/163;
427/165; 428/334; 428/336; 428/539
[51] Int. CI. B44 5/00; B32 3/10; B32 7/02
Field of Search 117/37 R, 38, 138.8 R,
117/138.8 PV, 138.8 UA, 70 A, 70 R, 69,
72, 73, 75; 161/146, 71 R; 350/61, 175;
351/62, 66

62 Claims, 16 Drawing Figures

An inorganic protective coating of a thickness of from 400 Å. to 5 microns is applied to a surface of an article at least the surface of which is formed of a synthetic resin to increase the surface hardness of the said article without any sacrifice in the inherent properties of the said article. The protective coating comprises discrete islands of an inorganic solid each having an area of at most 7×10^4 square microns and being firmly deposited on the synthetic resinous substrate, and being formed by evaporating an inorganic material through a shadow mask or screen onto the surface of the said article.

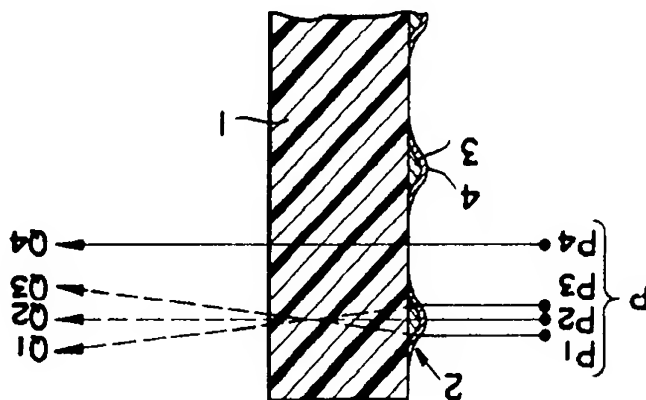
ABSTRACT

2,721,153	10/1955	Hopf et al.	117/38
3,044,438	7/1962	Oswald et al.	117/38
3,193,408	7/1965	Triller	117/38
3,271,180	9/1966	White	117/38
3,652,379	3/1972	White et al.	117/38 PV
3,672,925	6/1972	Feldstein	117/38

UNITED STATES PATENTS

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[95]



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Search Results - Record(s) 1 through 5 of 5 returned.**1. Document ID: US 5975173 A**

L14: Entry 1 of 5

File: USPT

US-PAT-NO: 5975173

DOCUMENT-IDENTIFIER: US 5975173 A

TITLE: Pneumatic tire using fiber composite material

DATE-ISSUED: November 2, 1999

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Izumoto; Ryuji	Tokyo			JP
Miura; Teruo	Tokyo			JP
Monji; Koshiro	Tokyo			JP
Iwasaki; Shinichi	Tokyo			JP
Fujino; Kentaro	Tokyo			JP
Ohashi; Masayuki	Tokyo			JP

US-CL-CURRENT: 152/209.4, 152/209.15, 152/209.18, 152/209.7, 152/458, 152/DIG.3

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC
Draw Desc	Image										

2. Document ID: US 5272198 A

L14: Entry 2 of 5

File: USPT

US-PAT-NO: 5272198

DOCUMENT-IDENTIFIER: US 5272198 A

TITLE: Asbestos-free microdenier acrylic fiber reinforced material for gaskets and the like

DATE-ISSUED: December 21, 1993

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Kaminski; Stanley S.	Stamford	CT		
Evans; Robert E.	Huntington	CT		

US-CL-CURRENT: 524/426, 277/650, 277/936, 428/373, 428/903, 442/351, 524/425, 524/445, 524/448, 524/449, 524/451, 524/525, 525/123, 525/232, 525/233, 525/238

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC
Draw Desc	Image										

(7) an amionic blend of methylene bishydroxyacetate, 33 percent by weight; sodium dimethyl-*p*-chlorophenylmethacrylate, 33 percent by weight; and sodium ethylene bis(hydroxycarboxylate), 33 percent by weight, (available as Amerstat 282 from New Industrial Division; AMIA-131 from Vinters Chemical Company); (6) sodium dichlorophene (G-4+40, available from Givaudan Corporation); and the like, as well as mixtures thereof; (C) cationic biocides, such as (1) cationic poly(oxyethylene dimethylamino)-ethylene (dimethylamino) ethylene dihydrochloride (Busan 77, available from Buckman Laboratories Inc.); (2) a cationic blend of methylenic bis(hydroxycarbonate and dodecyl guanidine hydrochloride (available as Siltme-Trol RX-31, RX-32, RX-32P, RX-33 from Betz Paper Chemical Corp.; (3) a cationic blend of a sulfonate, such as bis(trichloromethyl) sulfone and a quaternary ammonium chloride (available as Siltme-Trol RX-36 DFB-865 from Betz Paper Chem. Inc.); (4) a cationic blend of methylenic bis(hydroxycarbonate and chlorinated phenols (available as Siltme-Trol RX-40 from Betz Paper Chem. Inc.); and the like, as well as mixtures thereof. The biocide can be present in any effective amount; typically, the biocide is present in an amount of from about 0.1 percent by weight to about 3 percent by weight of the coating, although the amount can be outside this range.

Examples of the third ink receiving layer filler components include hollow microspheres, including Ecospheeres MC-37 (sodium borosilicate glass), Ecospheeres FTD 202 (high silica glass, 95 percent SiO₂), and Ecospheeres SI (high silica glass, 98 percent SiO₂), all available from Emerson and Cuming Inc.; Fillite 2007 (aluminum-silicate ceramic available from Fillite U.S.A.); Q-Cel 300 (sodium borosilicate available from Philadelphia Quartz); BZ3/500 (soda lime glass available from 3M Company); Clear B 10-0930 (phenolic polymers available from Union Carbide); Mitrilite 177 (vinylidene chloride-acrylonitrile available from Pierce & Stevens Chemical Corporation); and the like. Examples of solid microspheres include Spherglass E250P2 and 10002A (soda-lime glass-A-glass, B-glass), available from Porters Industries; Micro-F (soda-lime glass) available from D.J. Enterprises; ceramtic microspheres (available from Fillite U.S.A., and Zeculan Industries); glass beads, 3 to 10 microns, (#07666 available from Polymer Sciences Inc.); solid plastic microspheres available from Rohm & Haas, Dow Chemicals, Diamond Shamrock, and E.I. DuPont de Nemours & Company; hollow composite microspheres of polyvinylidene chloride/acrylonitrile copolymer shell, 15 percent by weight, and calcium carbonate, 85 percent by weight, available as Dualite M 6001 AE, and Dualite M 6017 AE from Pierce & Stevens Corporation; and the like. Mixtures of two or more types of microspheres can also be employed. Further information regarding microspheres is disclosed in, for example, *Encyclopedia of Polymer Science and Engineering*, vol. 9, pages 788 et seq., John Wiley and Sons (New York 1987), the disclosure of which is totally incorporated herein by reference; stearate coated calcium carbonate, available as Camet-CAL, Camet-CAL ST from Genstar Stone Products Company; sodium metasilicate anhydrous available as Drymet 59 from Crossfield Chemicals Incorporated; sodium metasilicate pentahydrate 38EV from Rhco Incorporated; magnesium carbonate available as Elastomag Tech Light, Elastomag Tech Heavy, Elastocat UF from Morton International; magnesium oxide available as Elastomag 100, Elastomag 100 R, Elastomag 100 K, Elastomag 100 L, Elastomag 100 M, Elastomag 100 N, Elastomag 100 O, Elastomag 100 P, Elastomag 100 Q, Elastomag 100 R, Elastomag 100 S, Elastomag 100 T, Elastomag 100 U, Elastomag 100 V, Elastomag 100 W, Elastomag 100 X, Elastomag 100 Y, Elastomag 100 Z, Elastomag 100 AA, Elastomag 100 AB, Elastomag 100 AC, Elastomag 100 AD, Elastomag 100 AE, Elastomag 100 AF, Elastomag 100 AG, Elastomag 100 AH, Elastomag 100 AI, Elastomag 100 AJ, Elastomag 100 AK, Elastomag 100 AL, Elastomag 100 AM, Elastomag 100 AN, Elastomag 100 AO, Elastomag 100 AP, Elastomag 100 AQ, Elastomag 100 AR, Elastomag 100 AS, Elastomag 100 AT, Elastomag 100 AU, Elastomag 100 AV, Elastomag 100 AW, Elastomag 100 AX, Elastomag 100 AY, Elastomag 100 AZ, Elastomag 100 BA, Elastomag 100 BB, Elastomag 100 BC, Elastomag 100 BD, Elastomag 100 BE, Elastomag 100 BF, Elastomag 100 BG, Elastomag 100 BH, Elastomag 100 BI, Elastomag 100 BJ, Elastomag 100 BK, Elastomag 100 BL, Elastomag 100 BM, Elastomag 100 BN, Elastomag 100 BO, Elastomag 100 BP, Elastomag 100 BQ, Elastomag 100 BR, Elastomag 100 BS, Elastomag 100 BT, Elastomag 100 BU, Elastomag 100 BV, Elastomag 100 BW, Elastomag 100 BX, Elastomag 100 BY, Elastomag 100 BZ, Elastomag 100 CA, Elastomag 100 CB, Elastomag 100 CC, Elastomag 100 CD, Elastomag 100 CE, 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3. Document ID: US 4871004 A

L14: Entry 3 of 5

File: USPT

US-PAT-NO: 4871004

DOCUMENT-IDENTIFIER: US 4871004 A

TITLE: Rubber containing aramid pulp reinforcement

DATE-ISSUED: October 3, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Brown; Robert J.	Cuyahoga Falls	OH		
Scriver; Richard M.	Atwater	OH		

US-CL-CURRENT: 152/209.4; 152/527, 152/548, 524/495, 524/514

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWIC

4. Document ID: US 3836412 A

L14: Entry 4 of 5

File: USPT

US-PAT-NO: 3836412

DOCUMENT-IDENTIFIER: US 3836412 A

TITLE: PREPARATION OF DISCONTINUOUS FIBER REINFORCED ELASTOMER

DATE-ISSUED: September 17, 1974

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Boustany; Kamel	Akron	OH		
Coran; Aubert Yaucher	Akron	OH		

US-CL-CURRENT: 156/62.2; 264/108, 264/109

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWIC

5. Document ID: JP 08127674 A

L14: Entry 5 of 5

File: JPAB

May 21, 1996

PUB-NO: JP408127674A

DOCUMENT-IDENTIFIER: JP 08127674 A

TITLE: ANTISTATIC RUBBER COMPOSITION

PUBN-DATE: May 21, 1996

INVENTOR-INFORMATION:

particular in situations wherein the ink image is dried by exposure to microwave radiation. (Generally, the term "cure" refers to the distance between the base line of the arc formed by the transparency or recording sheet when viewed in cross-section across its width (or shorter dimension, for example 8.5 inches in an 8.5x11 inch sheet, as opposed to length, or longer dimension, for example 11 inches in an 8.5x11 inch sheet) and the midpoint of the arc. To measure cure, a sheet can be held with the thumb and forefinger in the middle of one of the long edges of the sheet (for example, in the middle of one of the 11 inch edges in an 8.5x11 inch sheet) and the arc formed by the sheet can be matched against a pre-drawn standard template curve.

The transparencies of the present invention in embodiment-1 means exhibit little or no blocking. Blocking refers to the transfer of ink or toner from a printed image from one sheet to another when recording sheets are stacked together. The recording sheets of the present invention exhibit substantially no blocking under, for example, environmental conditions of from about 20 to about 80 percent relative humidity and at temperatures of about 80° F.

Further, the transparencies of the present invention in embodiment-1 exhibit high resistance to humidity. Resistance to humidity generally is the capacity of a recording sheet to control the blooming and bleeding of printed images, wherein blooming represents intra-diffusion of dyes and bleeding represents inter-diffusion of dyes. The blooming test can be performed by printing a bold filled letter such as "L" on a recording sheet and placing the sheet in a constant environment chamber preset for humidity and temperature. The vertical and horizontal spread of the dye in the letter "L" is monitored periodically under a microscope. Resistance to humidity limit is established when the dyes selected begin to diffuse out of the letter "L". The bleeding test is performed by printing a checker board square pattern of various different colors and measuring the inter-diffusion of colors as a function of humidity and temperature.

The optical density measurements recited herein were obtained on a Pacific Spectrograph Color System. The system consists of two major components, an optical sensor and a data terminal. The optical sensor employs a 6 inch integrating sphere to provide diffuse illumination and 8 degrees viewing. This sensor can be used to measure both transmission and reflectance samples. When reflectance samples are measured, a specular component may be included. A high resolution, full dispersion, grating monochromator was used to scan the spectrum from 380 to 720 nanometers. The data terminal features a 12 inch CRT display, numerical keyboard for selection of operating parameters and the entry of tristimulus values, and an alphanumeric keyboard for entry of product standard information.

Haze values recited herein were measured by a XL-211 Haze and Hazemeter supplied by Pacific Scientific Company. The lightfastness values of the ink jet images were measured in the Mark V Lightfastness Tester obtained from Microscopical Company, London, England.

The scrambled block copolymers and graft copolymers of the present application, such as methyl cellulose (MC)-polyacrylamide (PAm) copolymer with a methyl cellulose content of 51.7 percent by weight and a viscosity average molecular weight of $M_v=6.0 \times 10^5$, hydroxypropyl (HPC)-polyethylene oxide (PEO) copolymer with a hydroxypropyl cellulose content of 52.3 percent by weight and a viscosity average molecular weight of $M_v=1.8 \times 10^5$, Methyl cellulose (MC)-polyacrylic acid (PAA) copolymer with a

Embodiments of the present invention include a transparency comprised of a supporting substrate, a second cationic coating layer situated on the top of the first anionic coating layer comprised of an anionic polymer, and a first cationic coating layer situated on the top of the second cationic compounds and a lightfastness inducing agent, and a third compound of monomeric or polymeric cationic quaternary compounds, and a lightfastness inducing agent, and a third coating layer being comprised of a block polymer, a block and a filler, and wherein said transparency possesses a haze value of from about 0.5 to about 10 and a lightfastness value of from about 95 to about 99; a transparency comprised of a supporting substrate, thereover and thereunder a first coating layer comprised of an anionic polymer, a second cationic coating layer situated on the top of the first anionic layer, and a third layer receiving ink situated on the top of the second cationic layer and said third layer comprised of a mixture of two block or graft polymers wherein one component is more compatible with fast drying colored inks, and which first component is selected from the group consisting of nonionic

NAME
MIYAJI, KAZUO
OSAKI, TAKASHI

COUNTRY

INT-CL (IPC): C08 L 21/00; C08 K 3/04; C08 K 3/36; C08 K 7/06; C08 L 7/00; C09 K 3/16

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
Draw Desc	Image								

KWC

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Term	Documents
SILICA.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	363323
SILICAS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	13365
TYRE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	53766
TYRES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	22514
TIRE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	106106
TIRES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	41633
TIRE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	106106
TYRE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	53766
TYRES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	22514
TIRES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	41633
STYRENE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	234435
(SILICA AND (TYRE OR TIRE) AND STYRENE BUTADIENE AND ASPECT RATIO [AB]).USPT,PGPB,JPAB,EPAB,DWPI,TDBD.	5

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illustrative, and the other two are not representative, respectively, of the process parameters set forth in these conditions. The coatings, a total of six, are included on both surfaces or sides of the transparency unless otherwise indicated. All parts and percentages are by weight unless otherwise indicated.

[illegible]

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side by side

Hit Count Set Name
result set

DB=USPT,PGPB,JPAB,EPAB,DWPI,TDBD; PLUR=YES; OP=ADJ

<u>L17</u>	composit\$5 and silica and (tyre or tire) and styrene butadiene and aspect ratio [ab]	5	<u>L17</u>
<u>L16</u>	composit\$5 and silica and (tyre or tire) and styrene butadiene and aspect ratio [ti]	0	<u>L16</u>
<u>L15</u>	composit\$5 and silica and (tyre or tire) and styrene butadiene and aspect ratio	77	<u>L15</u>
<u>L14</u>	silica and (tyre or tire) and styrene butadiene and aspect ratio [ab]	5	<u>L14</u>
<u>L13</u>	silica and (tyre or tire) and styrene butadiene and aspect ratio [ti]	0	<u>L13</u>
<u>L12</u>	silica and (tyre or tire) and styrene butadiene [ti]	62	<u>L12</u>
<u>L11</u>	silica and (tyre or tire) [ti]	1787	<u>L11</u>
<u>L10</u>	11 and (tyre or tire)	0	<u>L10</u>
<u>L9</u>	L3 near12 aspect ratio	1	<u>L9</u>
<u>L8</u>	L3 near11 aspect ratio	0	<u>L8</u>
<u>L7</u>	L3 near15 aspect ratio	1	<u>L7</u>
<u>L6</u>	L3 near5 aspect ratio	0	<u>L6</u>
<u>L5</u>	L3 near aspect ratio	0	<u>L5</u>
<u>L4</u>	L3 and aspect ratio	58	<u>L4</u>
<u>L3</u>	1-60	6595	<u>L3</u>
<u>L2</u>	silica near aspect ratio and 1-60	0	<u>L2</u>
<u>L1</u>	silica near aspect ratio	10	<u>L1</u>

END OF SEARCH HISTORY

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Search Results - Record(s) 1 through 7 of 7 returned.**1. Document ID: US 20020036043 A1**

L9: Entry 1 of 7

File: PGPB

Mar 28, 2002

PGPUB-DOCUMENT-NUMBER: 20020036043
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020036043 A1

TITLE: Runflat tire having a rubberized insert containing 1,6-bis(N,N'-dibenzylthiocarbamoyldithio)-hexane

PUBLICATION-DATE: March 28, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
Victor Thielen, Georges Marcel	Schouweiler		LU	

US-CL-CURRENT: 152/517

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	FWOC
Draw Desc	Image									

2. Document ID: US 20020016404 A1

L9: Entry 2 of 7

File: PGPB

Feb 7, 2002

PGPUB-DOCUMENT-NUMBER: 20020016404
PGPUB-FILING-TYPE: new
DOCUMENT-IDENTIFIER: US 20020016404 A1

TITLE: NOVEL ELASTOMER COMPOSITE BLENDS AND METHODS - II

PUBLICATION-DATE: February 7, 2002

INVENTOR-INFORMATION:

NAME	CITY	STATE	COUNTRY	RULE-47
MABRY, MELINDA ANN	NEWTON	MA	US	
WANG, TING	BILLERICA	MA	US	
PODOBNIK, IVAN ZLATKO	HUDSON	NH	US	
SHELL, JAMES A.	SUWANEE	GA	US	
MORGAN, ALLAN CLARK	MANCHESTER	MA	US	
CHUNG, BIN	NASHUA	NH	US	
TOKITA, NOBORU	WOODBIDGE	CT	US	

US-CL-CURRENT: 524/495

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	FWOC
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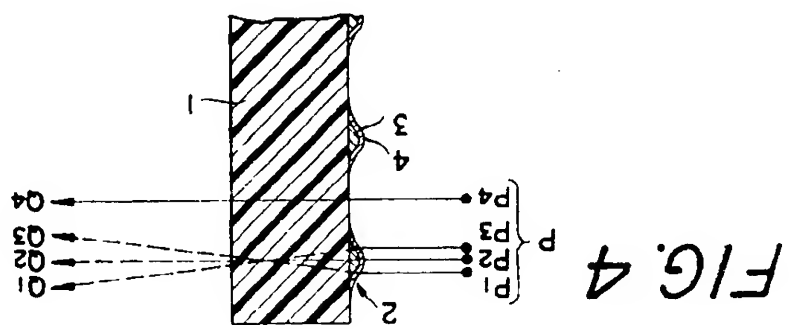


FIG. 4

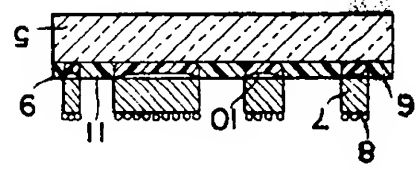


FIG. 5

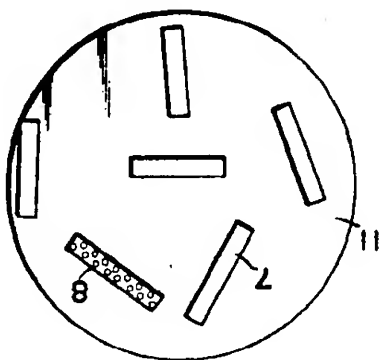


FIG. 6

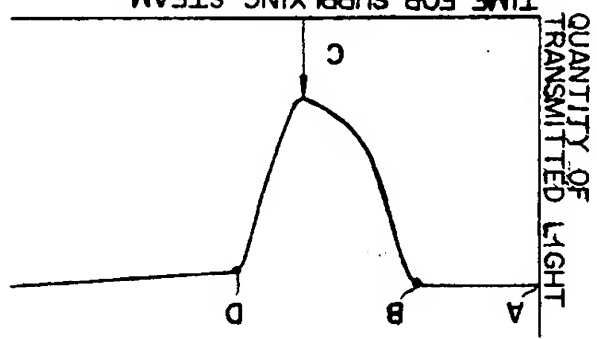


FIG. 7

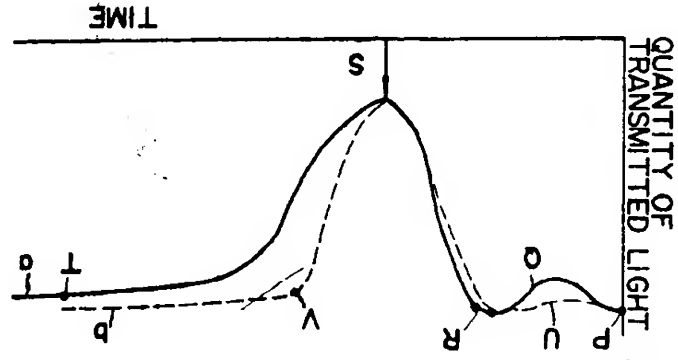


FIG. 8

TIME FOR SUPPLYING STEAM
TIME AFTER STOPPING THE SUPPLY

3. Document ID: US 6075084 A

L9: Entry 3 of 7

File: USPT

US-PAT-NO: 6075084

DOCUMENT-IDENTIFIER: US 6075084 A

TITLE: Elastomer composite blends and methods - II

DATE-ISSUED: June 13, 2000

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Mabry; Melinda Ann	Cleveland Heights	OH		
Wang; Ting	Billerica	MA		
Podobnik; Ivan Zlatko	Mason	NH		
Shell; James A.	Suwanee	GA		
Morgan; Allan Clark	Manchester	MA		
Chung; Bin	Nashu	NH		
Tokita; Noboru	Woodbridge	CT		

US-CL-CURRENT: 524/495; 524/496

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWIC
Draw Desc	Image									

4. Document ID: US 5558325 A

L9: Entry 4 of 7

File: USPT

US-PAT-NO: 5558325

DOCUMENT-IDENTIFIER: US 5558325 A

TITLE: Play balls or pressureless tennis balls

DATE-ISSUED: September 24, 1996

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Hargis; I. Glen	Tallmadge	OH		
Miranda; Richard A.	Berlin Center	OH		
Wilson; John A.	Akron	OH		
Yeoh; Oon H.	Hudson	OH		

US-CL-CURRENT: 473/606; 273/DIG.4, 273/DIG.5, 428/35.7, 428/36.4, 428/36.8

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWIC
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5. Document ID: US 5384355 A

L9: Entry 5 of 7

File: USPT

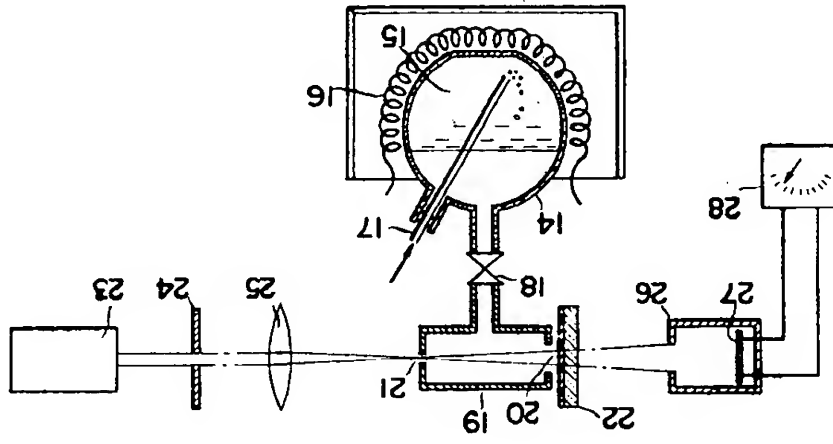


FIG. 12

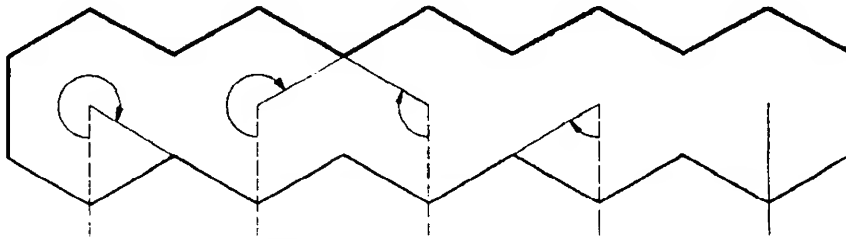


FIG. 10(b)

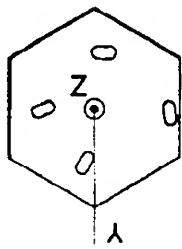


FIG. 10(a)

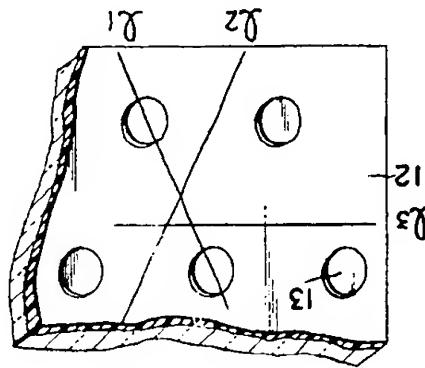


FIG. 9

US-PAT-NO: 5384355

DOCUMENT-IDENTIFIER: US 5384355 A

TITLE: Enhanced polymer concrete composition

DATE-ISSUED: January 24, 1995

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Allen; William C.	Pasadena	CA		

US-CL-CURRENT: 524/650; 524/493, 524/577, 524/8

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWIC
Draw Desc	Image									

6. Document ID: US 4871004 A

L9: Entry 6 of 7

File: USPT

US-PAT-NO: 4871004

DOCUMENT-IDENTIFIER: US 4871004 A

TITLE: Rubber containing aramid pulp reinforcement

DATE-ISSUED: October 3, 1989

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Brown; Robert J.	Cuyahoga Falls	OH		
Scriver; Richard M.	Atwater	OH		

US-CL-CURRENT: 152/209.4; 152/527, 152/548, 524/495, 524/514

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	KWIC
Draw Desc	Image									

7. Document ID: US 4323454 A

L9: Entry 7 of 7

File: USPT

US-PAT-NO: 4323454

DOCUMENT-IDENTIFIER: US 4323454 A

TITLE: Tube sheets for permeators

DATE-ISSUED: April 6, 1982

INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Fritzsche; Alfred K.	Cary	NC		
Holladay; Harry P.	Raleigh	NC		
Woodcock; Maurice L.	Raleigh	NC		

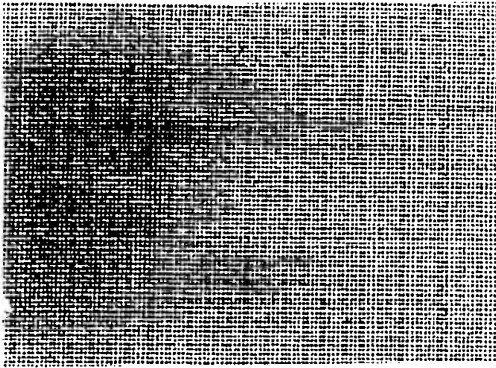


FIG. 15.

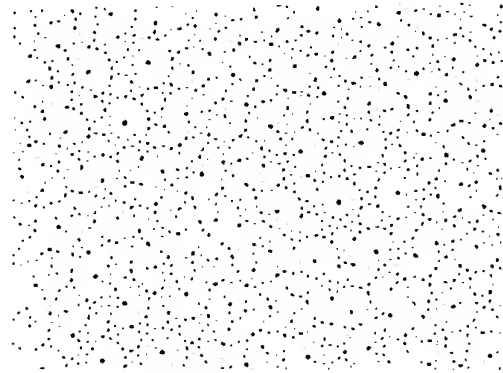


FIG. 14.

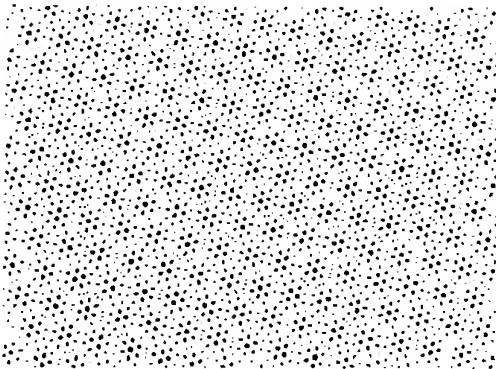


FIG. 13.

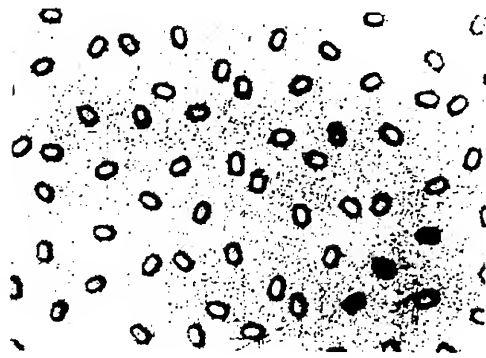


FIG. 11.

US-CL-CURRENT: 210/321.61; 210/321.88, 264/261, 264/263, 264/271.1, 264/328.14, 96/6,
96/8

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments
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Term	Documents
ASPECT.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	673506
ASPECTS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	345050
RATIO.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	1554720
RATIOS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	260783
STYRENE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	234435
STYRENES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	11603
BUTADIENE.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	127302
BUTADIENES.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	2383
SILICA.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	363323
SILICAS.DWPI,TDBD,EPAB,JPAB,USPT,PGPB.	13365
REINFORCING[USPT,PGPB]	116441
(ASPECT RATIO AND STYRENE BUTADIENE AND SILICA NEAR (REINFORCING AGENT OR FILLER) [CLM]).USPT,PGPB,JPAB,EPAB,DWPI,TDBD.	7

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of a hydrophobic polymer, the body loses its photo-transmissibility and, in addition, the aerosolized hydrophobic polymer layer cannot exhibit its deaggregating effect since it is completely isolated from the air by the continuous

ARTICLE AT LEAST SURFACE OF WHICH IS
FORMED OF A SYNTHETIC RESIN

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File: USPT

DOCUMENT-IDENTIFIER: US 6075084 A
TITLE: Elastomer composite blends and methods - II

Hlabey

Detailed Description Text (14):

Suitable elastomer latex fluids include both natural and synthetic elastomer latices and latex blends. The latex must, of course, be suitable for coagulation by the selected particulate filler and must be suitable for the intended purpose or application of the final rubber product. It will be within the ability of those skilled in the art to select suitable elastomer latex or a suitable blend of elastomer latices for use in the methods and apparatus disclosed here, given the benefit of this disclosure. Exemplary elastomers include, but are not limited to, rubbers, polymers (e.g., homopolymers, copolymers and/or terpolymers) of 1,3-butadiene, styrene, isoprene, isobutylene, 2,3-dimethyl-1,3-butadiene, acrylonitrile, ethylene, and propylene and the like. The elastomer may have a glass transition temperature (T_g) as measured by differential scanning calorimetry (DSC) ranging from about -120.degree. C. to about 0.degree. C. Examples include, but are not limited to, styrene-butadiene rubber (SBR), natural rubber and its derivatives such as chlorinated rubber, polybutadiene, polyisoprene, poly(styrene-co-butadiene) and the oil extended derivatives of any of them. Blends of any of the foregoing may also be used. The latex may be in an aqueous carrier liquid. Alternatively, the liquid carrier may be a hydrocarbon solvent. In any event, the elastomer latex fluid must be suitable for controlled continuous feed at appropriate velocity, pressure and concentration into the mixing zone. Particular suitable synthetic rubbers include: copolymers of from about 10 to about 70 percent by weight of styrene and from about 90 to about 30 percent by weight of butadiene such as copolymer of 19 parts styrene and 81 parts butadiene, a copolymer of 30 parts styrene and 70 parts butadiene, a copolymer of 43 parts styrene and 57 parts butadiene and a copolymer of 50 parts styrene and 50 parts butadiene; polymers and copolymers of conjugated dienes such as polybutadiene, polyisoprene, polychloroprene, and the like, and copolymers of such conjugated dienes with an ethylenic group-containing monomer copolymerizable therewith such as styrene, methyl styrene, chlorostyrene, acrylonitrile, 2-vinyl-pyridine, 5-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine, 2-methyl-5-vinylpyridine, alkyl-substituted acrylates, vinyl ketone, methyl isopropenyl ketone, methyl vinyl ether, alphasubstituted methylene carboxylic acids and the esters and amides thereof such as acrylic acid and dialkylacrylic acid amide. Also suitable for use herein are copolymers of ethylene and other high alpha olefins such as propylene, butene-1 and pentene-1.

Detailed Description Text (15):

The additional elastomer added during the dry mixing step of the wet/dry mixing method disclosed here can employ any elastomer or mixture of elastomers suitable to the intended use or application, including those listed above for use in the wet mixing step. In accordance with certain preferred embodiments, the elastomer latex employed in the wet mixing step is natural rubber latex and the additional elastomer employed in the dry mixing step is butadiene rubber (BR). In such preferred embodiments, the butadiene rubber preferably forms the minor phase or constituent of the elastomer composite blend, most preferably being from 10% to 50% by weight of total elastomer in the elastomer composite blend. In accordance with certain other preferred embodiments, the elastomer latex employed in the wet mixing step is natural rubber latex and the additional elastomer employed in the dry mixing step is styrene-butadiene rubber (SBR). In such preferred embodiments, the SBR preferably forms the major phase or constituent of the elastomer composite blend, most preferably being from 50% to 90% by weight of total elastomer in the elastomer composite blend. In accordance with certain other preferred embodiments, the additional elastomer is natural rubber. In accordance with certain other preferred embodiments, the elastomer latex employed in the wet mixing step is butadiene rubber latex and the additional elastomer employed in the dry mixing

regularly arranged circular elements, indicating the an-

isotropy in abrasion hardness.

(FIGS. 10(a) and 10(b)) show an example of forma-

tion of a pattern on a shadow mask to be employed in

the practice of the method of the present invention.

FIG. 11 is a microscopic photograph indicating an

example of an evaporating mask or shadow mask.

FIG. 12 is a rough sketch of an apparatus for determi-

nation of the anti-fogging property, and

FIGS. 13 to 15 show examples of patterns on the

masks for use in the formation of the protective coating

film in accordance with the present invention.

The shaped article to which a protective coating is

applied in accordance with the present invention may

be formed of any hydrophilic and hydrophobic poly-

mer. The hydrophobic polymers includes, e.g., polycar-

bonates, poly(methyl methacrylate), polyvinyl chlo-

ride, polystyrene, polypropylene, polyethylene and un-

saturated polyester resins. The hydrophilic polymers

includes, e.g., hydrophilic acrylate and methacrylate

polymers, polyvinyl alcohol, polyvinyl acetal, poly-

acrylamide, polyvinyl pyrrolidone, poly(cethylene ox-

ide), poly(cethylene imine), hydroxyethylcellulose and

regenerated cellulose. These materials may form

shaped bodies by themselves or form the surfaces of

shaped bodies of other plastics, glass, metal, wood,

there are preferably used water-insoluble, hydrophilic

acrylate and methacrylate polymers.

The hydrophilic acrylate and methacrylate polymers

are exemplified by, e.g., polymers of hydroxy-lower

alkyl acrylates, hydroxy-lower alkyl methacrylates, hy-

droxy-lower alkoxy-lower alkyl acrylates and hydroxy-

lower alkoxy-lower alkyl methacrylates, such as of 2

hydroxyethyl acrylate, 2-hydroxyethyl methacrylate,

diethylenglycol monoacrylate, diethylenglycol

monomethacrylate, triethylenglycol monoacrylate,

triethylenglycol monomethacrylate, 2-hydroxypropyl

acrylate, 2-hydroxypropyl methacrylate,

3-hydroxypropyl acrylate, 3-hydroxypropyl methacry-

ate, dipropylenglycol monoacrylate and dipropyleng-

lycol methacrylate.

The aforesaid polymer may be crosslinked, if neces-

sary, by copolymerization of 0.05 to 20, preferably 0.1

to 2.5% of a crosslinking agent, such as, e.g., ethylene-

glycol diacrylate, ethylenglycol dimethacrylate,

propylenglycol diacrylate, propylenglycol dimethac-

rylate, divinylbenzenes and

N,N'-methylene-bis-acrylamide.

By copolymerization with, e.g., acrylic acid, meth-

acrylic acid, itaconic acid, fumaric acid or mono-2-

hydroxypropyl itaconate.

As the polyvinyl alcohol there may be used partially

saponified polyvinyl acetate other than the complete

saponification product. The polyvinyl acetals includes

polyvinyl formal, polyvinyl acetoacetal, and polyvinyl

butyral. The polyacrylamides includes polymers of ac-

rylamide derivatives.

The protective coating film in accordance with the

present invention formed on a hydrophilic polymer

body combines the effect of enhancing surface hard-

ness and the advantages that there is no fear of scaling-

off and it is air permeable and photo transmissible.

Namely, the protective coating film of the present in-

vention on an article of which at least the surface is

formed of a hydrophilic polymer has a structure com-

prising discrete dots or stripes or otherwise figured is-

lands of an inorganic solid and openings or interstices

therebetween interconnecting the surface of the sub-

strate with the air; this structure prevents the scaling-

off of the protective coating film and deformation of

the film by thermal stress and allows gaseous molecules

to reach the surface of the hydrophilic polymer body.

The discrete structure should be of a pitch smaller than

the diameter of fibers of the cloth to be used for clean-

ing the surface or of abrasive grains. This structure is

obtainable by forming an inorganic protective coating

film through a sheet of perforated mask or combination

of several sheets of perforated mask on the surface of

a shaped body of which at least the surface is formed

of a plastic by an evaporating method, such as, e.g., re-

sistance heating method, electron beam method or

sputtering method.

In the resistance heating method, a material to be

evaporated is heated by Joule's heat generated by ap-

plication of an intensive electric current to a wire or

foil of a high melting point and the bond between the

protective coating and the substrate is attributable

mainly to physical adsorption and van der Waals

forces. In this case, since the bonding strength is not

sufficiently high, it is desirable to preheat the substrate

prior to evaporation or activate it by means of ion bom-

bardment to enhance adhesion.

In the electron beam method, the material is heated

by collision of a beam of a large number of electrons

accelerated to a high speed. In the sputtering method,

the material is bombarded by cations generated by

glow discharge, low pressure glow discharge in a mag-

netic field or high frequency electric field, low pressure

plasma, ion beam or like physical or chemical sputter-

ing means. In the electron beam method and sputtering

method, particles of a metal or metal oxide shot out of

a target have a very high level of energy (10 - 100 eV)

compared with particles evaporated in the resistance

heating method (about 0.2 eV), so that they locally

heat the surface of the substrate and form a substan-

tially complete chemical bond with the surface.

Therefore, through depending on the melting point

and decomposition point of the material being used, in

general it is preferred to process a material of a low

melting point in the resistance heating method and a

material of a high melting point in the electron beam

method. In all cases, however, the tem-

perature of the substrate should carefully be controlled

to prevent the substrate from thermal decomposition.

A fairly strong bond between the substrate and protec-

tive coating is attained by cleaning the surface of the

substrate by ion bombardment. This is believed to be

attributable to formation of oxygen linkages on the

polymer molecules.

The protective coating film may be formed by a

chemical method other than the above mentioned

physical methods.

A protective coating film of a desired percentage

area of openings or interstices and a desired pattern of

stripes or islands is made by use of a mask consisting of

one or several sheets of a masking sheet having numer-

ous through-holes having a desired contour or numer-

ous slits. The contour of through-holes or stripes and

their arrangement are not critical. It may be of discrete

step is SBR. In such preferred embodiments, the SBR preferably from 10% to 90% by weight of total elastomer in the elastomer composite blend. In accordance with certain other preferred embodiments, the elastomer latex employed in the wet mixing step is butadiene rubber latex and the additional elastomer employed in the dry mixing step is natural rubber. In such preferred embodiments, the natural rubber preferably is the minor constituent or phase of the elastomer composite blend, most preferably being from 10% to 50% by weight of total elastomer in the elastomer composite blend. In accordance with certain other preferred embodiments employing butadiene rubber latex in the wet mixing step, the additional elastomer is additional butadiene rubber. In accordance with certain other preferred embodiments, the elastomer latex employed in the wet mixing step is SBR and the additional elastomer is butadiene rubber. In such preferred embodiments, the butadiene rubber preferably is from 10% to 90% by weight of total elastomer in the elastomer composite blend. In accordance with certain other preferred embodiments, the elastomer latex employed in the wet mixing step is SBR and the additional elastomer is natural rubber. In such preferred embodiments, the natural rubber preferably is the major constituent or phase, most preferably being from 50% to 90% by weight of total elastomer in the elastomer composite blend. Certain other preferred embodiments SBR is employed in both the wet mixing and dry mixing steps, thus being essentially 100% of the elastomer in the elastomer composite blend.

Detailed Description Text (19):

When a carbon black filler is used, selection of the carbon black will depend largely upon the intended use of the elastomer composite blend. Optionally, the carbon black filler can include also any material which can be slurried and fed to the mixing zone in accordance with the principles disclosed here. Suitable additional particulate fillers include, for example, conductive fillers, reinforcing fillers, fillers comprising short fibers (typically having an L/D aspect ratio less than 40), flakes, etc. Thus, exemplary particulate fillers which can be employed in producing elastomer masterbatch in accordance with the methods and apparatus disclosed here, are carbon black, fumed silica, precipitated silica, coated carbon black, chemically functionalized carbon blacks, such as those having attached organic groups, and silicon-treated carbon black, either alone or in combination with each other. Suitable chemically functionalized carbon blacks include those disclosed in International Application No. PCT/US95/16194 (WO9618688), the disclosure of which is hereby incorporated by reference. In silicon-treated carbon black, a silicon containing species such as an oxide or carbide of silicon, is distributed through at least a portion of the carbon black aggregate as an intrinsic part of the carbon black. Conventional carbon blacks exist in the form of aggregates, with each aggregate consisting of a single phase, which is carbon. This phase may exist in the form of a graphitic crystallite and/or amorphous carbon, and is usually a mixture of the two forms. As discussed elsewhere herein, carbon black aggregates may be modified by depositing silicon-containing species, such as silica, on at least a portion of the surface of the carbon black aggregates. The result may be described as silicon-coated carbon blacks. The materials described herein as silicon-treated carbon blacks are not carbon black aggregates which have been coated or otherwise modified, but actually represent a different kind of aggregate. In the silicon-treated carbon blacks, the aggregates contain two phases. One phase is carbon, which will still be present as graphitic crystallite and/or amorphous carbon, while the second phase is silica (and possibly other silicon-containing species). Thus, the silicon-containing species phase of the silicon-treated carbon black is an intrinsic part of the aggregate; it is distributed throughout at least a portion of the aggregate. It will be appreciated that the multiphase aggregates are quite different from the silica-coated carbon blacks mentioned above, which consist of pre-formed, single phase carbon black

Detailed Description Text (22):

Selection of the particulate filler or mixture of particulate fillers will depend largely upon the intended use of the elastomer composite blends. As used here, particulate filler can include any material which can be slurried and fed to the mixing zone in accordance with the principles disclosed here. Suitable particulate fillers include, for example, conductive fillers, reinforcing fillers, fillers comprising short fibers (typically having an L/D aspect ratio less than 40), flakes, etc. In addition to the carbon black and silica-type fillers mentioned above, fillers can be formed of clay, glass, polymer, such as aramid fiber, etc. It will be within the ability of those skilled in the art to select suitable particulate fillers for use in the method and apparatus disclosed here given the benefit of the present disclosure, and it is expected that any filler suitable for use in elastomer compositions may be incorporated into the elastomer composites using the teachings of the present disclosure. Of course, blends of the various particulate fillers discussed herein may also be used

islands or stripes and arranged regularly or at random. The area of each preferably is 7×10^3 square microns or less, more desirably 3×10^3 square microns or less, because if it exceeds 3×10^3 square microns transmission of light becomes nonuniform and there occasionally occurs fluctuation of transmitted light and the coating film becomes fragile. In particular in case of hydrophilic polymer bodies, it is preferred that the area to be 8×10^3 square microns or less from the point of view of non-fogging and hygroscopicity. The thickness of the aforementioned coating consisting of numerous discrete islands preferably is 400 angstroms to 5 microns, because a film of a thickness of less than 400 angstroms does not have sufficient function and, on the other hand, one of a thickness exceeding 5 microns has a haze and is poor in adhesion to the substrate.

The shape or contour of each element of the protective coating film may be circle, oval or stripe, though it is preferred that the ratio of its short axis to its long axis ranges between 0.1 and 1.0.

It is preferred that openings or interstices between islands or stripes be uniformly distributed throughout the surface to be protected. The percentage area of openings may be varied depending on desire, though normally is 5 to 99%. In case of a hydrophilic polymer body, a percentage area of openings of 30 to 99% is preferred to attain the object of surface protection without sacrifice in the desirable properties of the body, and, in case of a hydrophobic polymer body, a range from 5% to 70% is preferred because, in the latter cases, the protective coating is applied for the purpose of surface protection only.

The term "percentage area of openings" means the percentage of an area obtained by subtracting the total area of islands from the total area of the substrate covered by the protective coating. Usually, for instance, it is represented by the following equation in the case of a two-dimensional zig-zag pattern.

$$S (\%) = (1 - 2\pi r^2 / \sqrt{3} l^2) \times 100$$

where S is the percentage area of openings, r is the diameter of an island and l is the average distance between two adjacent islands.

As the result of more detailed experiments, we have found that, in case of hydrophilic polymer bodies, the anti-fogging property takes its highest value when the percentage area of openings is in the range of from 60 to 99%.

In the theoretical point of view, it is believed that, when the aforementioned protective coating film is applied to the surface of a hydrophilic polymer, the anti-fogging property deteriorates as the total area of the islands increases. In other words, the percentage area of openings decreases, whereas, surprisingly, it has been found that, as the result of experiments as indicated by FIG. 1, a coated body having a protective coating film of a percentage area of opening of 60 to 99% is superior in anti-fogging property to one of a percentage area of opening of 100% (a body having no protective coating film). The hump of the curve in FIG. 1 indicates this.

The curve in FIG. 1 is obtained by plotting the anti-fogging property I/I_0 vs. the percentage area of openings, as determined by the method as set forth hereinafter on coated bodies prepared by evaporating silicon oxide through various masks on to substrates to form thereon a protective coating film of a thickness of 1,000 to 1,500 angstroms. The percentage area of

openings is determined by measuring the total area of islands by microscopic photography, since the pattern of the protective film is not always identical with that of the mask used because of imperfect contact between the surface of the substrate and the mask.

Thus, the present invention is based on the discovery contrary to the ordinary idea that an uncoated hydrophilic plastic body is superior in non-fogging property to an at least partially coated one. While the exact mechanism is uncertain, it is believed that diffusion of water deposited on the surface into the inside of the hydrophilic plastic body is delayed by the porous protective coating film and this delay results in an enhancement of the anti-fogging property.

In the practice of the present invention there may be used various inorganic substances in the formation of a protective coating film, and for the formation of a transparent protective coating film there are used oxides, nitrides, fluorides and sulfides of various metals.

The material may be applied to a substrate in an appropriate process according to the material used.

For example, the material suitably applied in the resistance heating method includes, e.g., tin oxide, cadmium oxide, indium oxide, zinc oxide, bismuth oxide, antimony oxide, silicon monoxide, cadmium sulfide, zinc sulfide, magnesium fluoride, beryllium fluoride, calcium fluoride, lithium fluoride, sodium fluoride, lithium fluoride, cerium fluoride and cryolite.

The material suitably applied in the electron beam or sputtering method includes, e.g., thorium oxide, beryllium oxide, calcium oxide, strontium oxide, barium oxide, aluminum oxide, magnesium oxide, zirconium oxide, cerium oxide, silica, niobium oxide, titanium oxide, tantalum oxide, lanthanum oxide, hafnium oxide, niobium nitride, boron nitride, aluminum nitride and silicon nitride.

Both transparent and opaque materials are employed in accordance with the object to form a protective coating film of the present invention, but when a transparent protective coating film is formed on a transparent substrate, there is sometimes observed the phenomenon of becoming cloudy due to scattering of light, so called haze. It is desired to avoid development of haze in the case especially of lenses. The haze is attributable to scattering of light at the periphery of or center of each element or island of a protective coating film.

Referring to FIG. 2, discrete elements or islands 2 are fixed to the surface of a substrate 1 having a relatively low surface hardness. In rays P incident upon the body, rays P₁ and P₂ go right on after passed through the body and arrive at Q₁ and Q₂, respectively, namely unscattered and developing no haze, while rays P₃ and P₄ are refracted at Q₁ and Q₂, respectively, since they are refracted on the surface of the body. This is a reason for the development of haze in the transparent body. This results in the drawback that the visibility through the body is hindered somewhat though the surface hardness of the body is enhanced to a great extent by application of a discrete protective coating film thereto which is free from cracking and scaling-off.

As the result of further investigations, we have discovered that these drawbacks are eliminated by the following means.

In accordance with the present invention, haze is minimized by use as the coating material of an inorganic solid having a high hardness and a relatively low transparency, by first applying a discrete coating film

CLAIMS:

16. The method of producing elastomer composite blend in accordance with claim 11 wherein the additional particulate filler is silica.

of an inorganic solid having a high tensile strength and a high adhesion to a substrate and applying thereover a solid having a relatively low modulus of elasticity and a blend of such high transparent and low transparent solids.

Illustrating in more detail, for instance, hitherto there has been used for forming a protective coating film silicon dioxide SiO_2 as a material having high transparency and hardness and excellent adhesion to a plastic substrate. In accordance with the present invention, haze is minimized to a great extent by applying a mixture of a small amount of a metal and SiO_2 or by applying a material having a low transmittance, such as, e.g., metallic aluminum, chromium or like material, over a coating of SiO_2 so as to reduce transmittance.

Namely, the present invention is characterized by reducing the quantity of transmitted light thereby to reduce the quantity of scattered light causing the haze by reducing the transmittance of the discrete protective coating film applied to a substrate so as to enhance surface hardness.

Illustrating the present invention referring to FIG. 3 and 4, to a substrate 1 to be protected there are applied elements 2 of a protective coating film consisting of a material having a low transmittance. The quantities of rays of light P_1 , P_2 and P_3 arrived at O_1 , O_2 and O_3 are reduced or minimized to zero by the element, so that rays P_1 predominate in transmitted light through the body whereby haze is minimized to a great extent. In the embodiment as illustrated by FIG. 4, to a substrate 1 there is applied a transparent material 3 and thereover an opaque material 4 to form elements 2 of a protective coating film. In this case, in incident rays P_1 to P_3 only pass through the body whereby haze is reduced to a great extent.

That is to say, the present invention intends to minimize haze by cutting off scattered light and allowing straight-forward light only to pass the body, so that the order of the transparent material 3 and opaque material 4 in FIG. 4 may be reversed, and the same result can be obtained by applying the opaque material annularly only to the peripheral section of each element or island of the transparent material. It is necessary for eliminating haze by minimizing or eliminating scattered light to reduce the transmittance of each element to 50% or less, preferably to 30% or less.

In the practice of the present invention there may be used the various transparent materials mentioned above for forming elements of a protective film and, on the other hand, there may be used as the opaque material to be used in combination with the transparent material, materials such as chromium, nickel, aluminum, gold, silver, tantalum, titanium or like metals; iron oxides, chromium oxide, cobalt oxide and like colored metallic oxides; and niobium nitride, chromium nitride, titanium nitride and like nitrides and carbides, silicides, fluorides and like so called refractories.

In the present invention, the protected areas of the surface of a substrate increase as the density of elements or islets scattered as to form a protective coating layer increase, while, on the other hand, the percentage area of openings on the substrate decreases to hinder the inherent desirable properties of the substrate, such as, e.g., hygroscopicity and the anti-fogging property in case of a hydrophilic resin. The present invention is of great value for enhancing the surface hardness of a shaped body of a hydrophilic plastic having insufficient

surface hardness, so that the present invention will be illustrated hereinafter in more detail with reference to such a substrate, but of course, the present invention is applicable to any substrate in principle.

As shown in FIGS. 5 and 6, when each element or islet 7 formed on a substrate 5 and a coating layer 6 of a hydrophilic resin has a large area, there are formed water droplets 8 on the surface of each element due to lack of hygroscopicity of the protective coating itself to yield local fog upon exposure to steam or water vapor. To avoid this phenomenon it is desirable that each element has as small an area as possible. This is true of dehumidification of a hydrophilic plastic body after absorption of water. Namely, water 10 absorbed by plastic 9 just under an element 7 of a protective coating film must diffuse in the plastic layer to the naked section 11 to vaporize into the air. On this occasion, it is desirable for quick vaporizing of moisture that the area of each element 7 is as small as possible, because if moisture absorbed by the plastic just under an element 7 stays there indefinitely the element gives a faulty dehumidification response. The dehumidification response will be illustrated in detail with reference to FIG. 7.

FIG. 7 shows the change in quantity of light transmitted through a specimen of a hydrophilic or hygroscopic plastic layer having no protective coating film thereon determined by supplying steam at a constant flow rate thereto and continuing measurement after stop of the supply of steam. A laser beam is directed at a point of the surface of the plastic layer while supplying the steam. In the initial stage of supply of steam, the transmittance of the plastic layer for the laser beam passing straight through the specimen is not varied at all because of adsorption of steam by the hygroscopic resin. During continuous supply of steam for a long time, the resin is saturated with moisture, and thereafter there occurs condensation of a portion of the steam on the surface to form water droplets which cause fog. With progress of the condensation of steam, the quantity of light received by a light detector located on the optical axis of the laser beam is gradually decreased by scattering with the water droplets. In FIG. 7 the quantity of transmitted light arrived at the receiver is plotted as ordinate and the time of supply of steam as abscissa. In the graph, from point A to B there is no change in the quantity of transmitted light as steam is absorbed by the specimen so as not to form any water droplets thereon, while from point B to C the quantity decreases abruptly because of formation of fog on the surface, after the resin being saturated by moisture. When the supply of steam is stopped at point C, the quantity increases gradually thereafter because of evaporation of the water droplets into the air and the specimen reverts to the original transparent state at point D. The time elapsed from the point A and B is the value indicating the anti-fogging quality or property and the value represented by the time elapsed between the point C and D indicates dehumidification response.

In case of a specimen prepared by evaporating silicon dioxide onto a hydrophilic polymer sheet through a stainless steel mask having numerous circular through holes each of 100 microns ϕ at pitches of 200 microns to form a coating of a thickness of 200 angstroms consisting of discrete circular elements each of a diameter of about 100 microns, the quantity of transmitted light varies as indicated by the curve α (full line), in FIG. 8

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result set*DB=USPT,PGPB,JPAB,EPAB,DWPI,TDBD; PLUR=YES; OP=ADJ*

<u>L13</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) and (nm or nanometer or micron)[clm]	7	<u>L13</u>
<u>L12</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) and (nm or nanometer or micron)[ab]	1	<u>L12</u>
<u>L11</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) and (nm or nanometer or micron)[ti]	0	<u>L11</u>
<u>L10</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) and (nm or nanometer or micron)	25	<u>L10</u>
<u>L9</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) [clm]	7	<u>L9</u>
<u>L8</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) [ab]	2	<u>L8</u>
<u>L7</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler)	39	<u>L7</u>
<u>L6</u>	aspect ratio and styrene butadiene and silica near (reinforcing agent or filler) [ti]	0	<u>L6</u>
<u>L5</u>	(particle size and aspect ratio) and styrene butadiene and silica near (reinforcing agent or filler) [ti]	0	<u>L5</u>
<u>L4</u>	(particle size or aspect ratio) and styrene butadiene and silica near (reinforcing agent or filler) [ti]	3	<u>L4</u>
<u>L3</u>	styrene butadiene and silica near (reinforcing agent or filler) [ti]	24	<u>L3</u>
<u>L2</u>	silica near (reinforcing agent or filler) [ti]	702	<u>L2</u>
<u>L1</u>	silica near (reinforcing agent or filler)	8281	<u>L1</u>

END OF SEARCH HISTORY

A flat glass plate of 3 mm x 50 mm x 50 mm was cleaned and coated with a hydrophilic polymer, polyvinyl alcohol (PVA), in a thickness of about 5 microns. After fully drying the coating, the plate was set in a vacuum evaporation chamber. In this case, there was employed a combined mask consisting of three stainless steel panels each having circular holes of 300 microns ϕ arranged in a pattern as shown in FIG. 9 at a pitch

EXAMPLE 6

As indicated by the above Table, the protective films in accordance with the present invention enhanced the abrasion resistance without sacrifice in the non-fogging quality and transparency.

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	160	50
Coated 500 A	150	500
Coated 3,000 A	170	Above 1,000

Table 2

Two glass plates each of 50 mm x 50 mm x 3 mm were coated with a 2-hydroxyethyl methacrylate polymer (Hydron) respectively to form thereon a coating film of a thickness of 23 microns and, after drying, the coated surface of each plate was covered with a square section mask consisting of an 100 mesh standard wire netting and set in a vacuum evaporating chamber. An electric current was applied to a molybdenum boat containing therein silicon monoxide and located below the plate in the chamber after evacuation of the chamber to 2×10^{-5} Torr to form a discrete coating of silicon monoxide of 500 A. on one of the plates and of 3,000 A. on the other plate. The specimens were subjected to determination of the non-fogging quality and the abrasion test.

The results of the tests were summarized in the following Table 2 in comparison with the properties of an uncoated Hydron surface. The percentage area of openings of the protective coating on the two specimens was about 60%.

EXAMPLE 5

As indicated by the above Table, the protective films in accordance with the present invention enhanced the abrasion resistance to a great extent without sacrifice in the non-fogging quality. The transparency of the lenses remained unchanged.

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	20	50
Coated	22	200

Table 1

film thus obtained was about 55%.

1 in comparison with those on an uncoated Hydron surface. The percentage area of openings of the protective film thus obtained was about 55%.

1 in comparison with those on an uncoated Hydron surface. The percentage area of openings of the protective film thus obtained was about 55%.

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated	18	50
Coated	6	Above 1,000

Table 4

To a surface of a glass plate of 50 mm x 50 mm x 3 mm there was applied a 2-hydroxyethyl methacrylate polymer (Hydron) in a thickness of 5 microns and, after drying, the Hydron-coated surface was closely covered by a stainless steel mask having a number of slits of a width of 500 microns at a pitch of 700 microns. The plate was subjected to evaporation of silicon monoxide in the same manner as in Example 1 to form thereon a coating film of a thickness of 3,000 A. and a percentage area of openings of about 30%. The results of the non-fogging test and abrasion test on the specimen were as shown in the Table 4.

EXAMPLE 8

The refractive index of PVA is usually 1.49 to 1.53, that of the PVA used in the above Example was about 1.51, so that the discrete protective film could be observed with careful observation because Bi_2O_3 has a high refractive index of 2.42. According to the field of application, it is desirable to make the protective film invisible, so that, in this Example, there was used a windshield glass having a substantially identical refractive index of 1.52. The glass plate was coated with a PVA as used in Example 6 and then coated with a mask film, which is used usually as a windshield, using a mask as used in Example 6 under a vacuum of 1×10^{-6} Torr with the aid of an electron beam of 20 mA accelerated by a voltage of 4 KV. The distance between the source and the surface of the substrate was 120 mm and the evaporating time was about 1 minute. On the PVA surface it was difficult to confirm the presence of a discrete coating film. The thickness of the coating film was 1,500 A. and the percentage area of openings was 80%. When subjected to the abrasion test, there was observed no scratch even after brushing 500 times and it was ascertained that the non-fogging quality is not hindered at all as indicated by fogging after exposure of about 23 seconds in the fogging test.

EXAMPLE 7

Specimen	Non-fogging quality (sec)	Abrasion test
Uncoated PVA	20	5
Coated PVA	18	300

Table 3

unprotected PVA film for comparison to obtain the results summarized in the following Table 3. The percentage area of openings of the protective film was 80%.

unprotected PVA film for comparison to obtain the results summarized in the following Table 3. The percentage area of openings of the protective film was 80%.